THE BRONZE AGE OBJECTS FROM TEL NAMI, ISRAEL: THEIR CONSERVATION AND IMPLICATIONS FOR ANCIENT METALLURGY IN THE EASTERN MEDITERRANEAN

A Thesis

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ABSTRACT

The Bronze Age Objects from Tel Nami, Israel:
Their Conservation and Implications for Ancient Metallurgy
in the Eastern Mediterranean. (August 1991)
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This thesis investigates the conservation of bronze objects from Tel Nami, Israel. Since Tel Nami is located on the Mediterranean coast, two problems are central to this investigation: the destructive nature of cuprous chloride from seawater inundation, and the stabilization of the bronze artifacts from subsequent corrosion attack.

An examination of the internal structure of metal and Bronze Age metallurgy technology of copper and its alloys provides a basis for understanding how corrosion operates in ancient metal. Furthermore, this study examines the unique combination of factors which comprise a marine coastal site in order to determine how they contribute to in-situ corrosion processes. The final assessment of the conservation project includes a discussion of the methodology and current existing technology. This is followed by the utility of conservation in providing important diagnostic information about artifacts and implications for future research.

ACKNOWLEDGEMENT

I would like to express my appreciation to my Committee Chairman, Dr. D.L. Hamilton, for his support and inspiration. He was my expert guide and mentor throughout my entire journey at Texas A&M University. Under his tutelage, I learned the basics of archaeological conservation and gained a solid foundation in archaeological fieldwork. His emphasis on good common sense and resourcefulness have instilled in me the importance of combining both a scholarly and practical approach to archaeology.

I would also like to thank the rest of my outstanding committee members. Dr. Bruce Dickson has been a mentor in the truest sense of the word. To him, I express my deep gratitude for his continual support and encouragement and ever-present wit. As his student, I have grown by leaps and bounds since coming to Texas A&M. For this, and many other reasons, I cannot thank him enough.

I would like to especially thank Dr. Michal Artzy for her support and friendship, and for teaching me about the Late Bronze Age. I will always be grateful to her for having faith in my ability to carry out this thesis project. Without her, this thesis would not have been possible.

Dr. George F. Bass has made Mediterranean archaeology come alive in the past twenty years, and through his efforts, has inspired many of us to step into the discipline. I would like to thank him for this inspiration and for the helpful suggestions that he contributed toward the writing of this thesis.

I would also like to especially thank Dr. Vaughn Bryant, Head of the Department of Anthropology at Texas A&M, for his encouragement from the very beginning of my graduate career. Dr. Gentry Steele and Dr. Norbert Dannhaeuser, through their friendship and guidance, have been instrumental in my development as an anthropologist. I extend a word of thanks to the College of Liberal Arts for their support for research and the Samuel H. Kress Foundation for their generous contribution to my Masters Thesis project.

This acknowledgement would not be complete without special thanks to various friends who have contributed to my academic career in one way or another. I would like to thank Diana Thornton for teaching me WordPerfect and computer literacy, and Wayne Smith for taking over where Diana left off after she moved away. Many thanks to Helen Dewolf and Charles Moore for providing two figures for this thesis.

Finally, my life in College Station has been enriched through the kindness, generosity and friendship of Dr. Lyle Schoenfeldt and Wanda Hinshaw. To them, I am eternally grateful. Last, but not least, I would like to thank my mother for always having an unconditional belief in my goals and aspirations, and to my good friend Miguel Paredes, who encouraged me to come to College Station to seek out a dream.

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CHAPTER I

INTRODUCTION AND SITE DESCRIPTION

Background

Since 1987, I have been involved with the Tel Nami Regional Project, which is directed by Dr. Michal Artzy of the Center for Maritime Studies and Institute of Archaeology at Haifa University, Israel.

In my first two seasons there, I participated in field excavation, serving as Pottery Registrar in 1987. In 1988, a sizable number of bronze artifacts was discovered at the site. Many of these artifacts were found in a remarkable state of preservation, while others were highly mineralized. It was crucial that a comprehensive conservation program be implemented for stabilizing the bronzes, particularly since they had been exposed to the corrosive effects of seawater for thousands of years. Late in 1988, I received permission from Dr. Artzy to design and carry out a conservation program which was to be conducted at Haifa University, as part of my Masters Thesis project.

In the Spring of 1989, I received a grant from the Samuel H. Kress Foundation. Through this grant, I was able to establish a conservation laboratory at Haifa University as part of the conservation program to clean and stabilize the artifacts. Laboratory conservation began in August, and included artifacts of ivory,

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This thesis follows the style and format of American Antiquity.

silver, faience, bronze and ceramic materials.

While the bulk of my project is directed toward the conservation of bronze, three other topics have been included. It was intriguing that many of the Tel Nami bronzes were so well-preserved, a point Dr. Artzy and I discussed on several occasions. From these discussions, I determined that no criteria existed for what constitutes a marine coastal site and how the micro-environment at this type of site relates to in situ corrosion processes. Dowman (1970) and Rose (1975) have defined and discussed the micro-environment of land sites, and Pearson (1987) has provided an excellent study on the underwater environment. From these studies and my own experience at Tel Nami, I was able to break the micro-environment into components, and then see how it contributed as a whole to cuprous metal corrosion.

It was important to see whether any patterns would emerge from this research and what forces caused the pitting, cracking and heavy corrosion crusts found on some of the artifacts. This necessitated a complete discussion of metal corrosion to understand the corrosion processes taking place in a marine coastal environment.

This research would not be complete without investigating ancient metallurgy technology because metalworking and production influence the internal structure and corrosion behavior of ancient metals. Thus, a chapter on this topic is included as well. From these perspectives, a discussion of the existing conservation technology is more complete.

Site Description

The archaeological site of Tel Nami is situated on a peninsula, about 15 km south of Haifa, Israel, near Kibbutz Newe Yam. The peninsula forms part of a partially-submerged sandstone (kurkar) ridge, one of three such longitudinal ridges which run parallel to the Carmel mountain range (Ronen 1983:121) (Figure 1). This peninsula comprises part of a larger settlement which extends east and north of the peninsula, under the coastal dunes, as well as southeast to an agricultural area, about a kilometer away. While the overall settlement is quite large, only the tell and Nami East have been excavated (Figure 2). The tell, which rises approximately nine meters from base to summit, presently consists of three main areas: Areas G, D1 and D. The tell is connected to Nami East by a sandy tombolo which is about 100 m wide. Nami East is characterized by sand dunes and is bordered by modern fish ponds which were either a swamp or brackish lake in antiquity. The excavated section at Nami East has been designated as Area O (Figure 3).

The periods of settlement on the tell and the surrounding areas can be dated to the second millennium B.C., mainly the Middle Bronze IIB (MB) possibly Late Bronze (LB) IIA, and definitely Late Bronze IIB. The chronology of the Bronze Age in the Levant is largely determined by the absolute dating of the Egyptian king lists beginning about 3100 B.C. (Moorey 1981:79-80). Cross-dating comes from datable contexts in Egypt where imported ceramics from Palestine have been found, and from Egyptian objects such as scarab seals and royal inscriptions which have been recovered in Syro-Palestine. The chronological sequence chosen for this thesis is based on Mazar's recent revisions (1990:10), presented in Table 1.

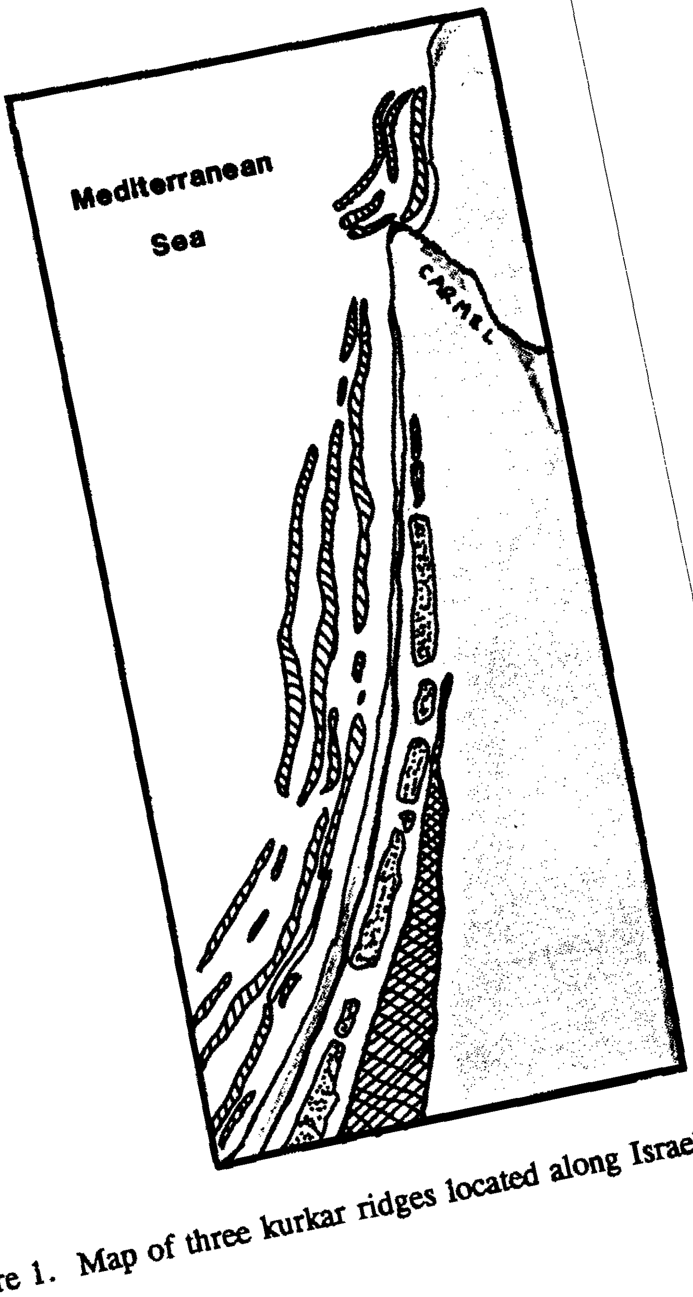


Figure 1. Map of three kurkar ridges located along Israel's coast (after Neev 1987:4).

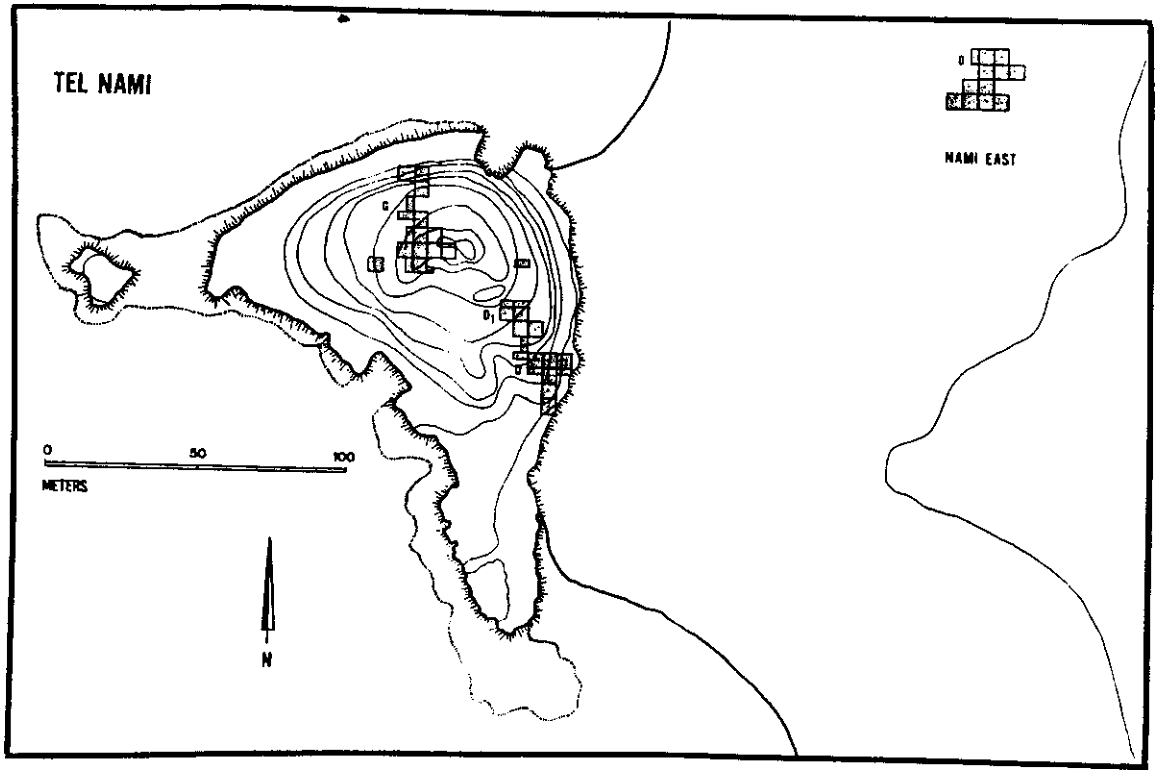


Figure 2. Map of Tel Nami.

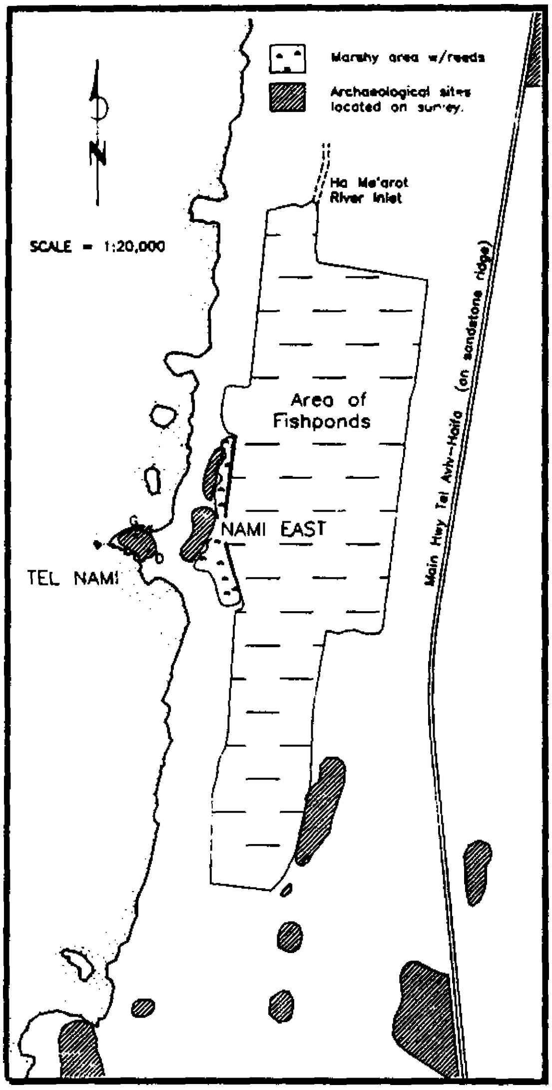


Figure 3. Map of the site showing Nami East (from Jacobsen 1988:12).

Table 1. Chronology for the archaeological periods of ancient Israel (after Mazar 1990:10).

Pre-Pottery Neolithic A	ca. 8500 - 7000 B.C.
Pre-Pottery Neolithic B	ca. 7500 - 6000 B.C.
Pottery Neolithic A	ca. 6000 - 5000 B.C.
Pottery Neolithic B	ca. 5000 - 4300 B.C.
Chalcolithic	ca. 4300 - 3300 B.C.
Early Bronze I	ca. 3300 - 3050 B.C.
Early Bronze II-III	ca. 3050 -2300 B.C.
EB IV/Middle Bronze I	ca. 2300 - 2000 B.C.
Middle Bronze IIA	ca. 2000 - 1800/1750 B.C.
Middle Bronze IIB-C	ca. 1800/1750 - 1550 B.C.
Late Bronze I	ca. 1550 - 1400 B.C.
Late Bronze IIA-B	ca. 1400 - 1200 B.C.
Iron IA	ca. 1200 - 1150 B.C.
Iron IB	ca. 1150 - 1000 B.C.
Iron IIA	ca. 1000 - 925 B.C.
Iron IIB	ca. 925 - 720 B.C.
Iron IIC	ca. 720 - 586 B.C.

The first survey carried out by Dr. Artzy in 1985, was intended as an investigation of a small, ancient fishing village, but winter storms during 1985-1986 revealed a patch of dark soil which contained sherds dating to the Late Bronze Age, including a sherd of imported Cypriot White Slip Ware. All this lead to something more international in scope than a small fishing village. The first opportunity to investigate this area, named Nami East, came during the summer of 1986, the first official field season under Dr. Artzy's direction.

A test trench dug in Nami East during the summer field season of 1987 revealed a substantial structure with walls over a meter in thickness, connected to a drainage system. Discovery of graves, plus structures on the tell during that same season confirmed that this was a settlement whose occupants were involved in the international maritime trade of the Middle and Late Bronze Age. The fishponds and large sand dunes covering Nami East have made it difficult to determine the actual size of the settlement, but aerial photographs and jettings done for geomorphological studies of the area indicate it to be much larger than previously thought.

Tel Nami can be considered as part of a string of settlements that dotted the Carmel Coast. Based on evidence recovered from submerged sites in the area, coastal settlement dates back to the seventh millennium B.C. (Pre-Pottery Neolithic) (Raban 1981:288-289, Raban and Galili 1985:326).

During the first half of the Early Bronze Age, small, spread-out villages, were established near lagoon or river outlets along the coast (Raban 1985:14). It appears that settlement then concentrated inland during the latter part of the Early Bronze Age in the Shepelah and mountain regions (Gophna 1984:29). Cities such as Megiddo and Arad were established on hilltops, most likely for defense purposes (Rosen 1986:16) (Figure 4).

The MB IIA period, unlike the Early Bronze Age, represents a time of large-scale and intensive settlement of the coastal plain (Gophna and Portugali 1988:225, Herzog 1988:92). Byblos in northern Syria, and Akko in northern Israel are notable coastal settlements for this period. Many of these Middle Bronze Age settlements were located close to an estuary or river outlet. The inhabitants chose their sites wisely, taking advantage of locales adjoining arable land, perennial water sources and access to the main longitudinal highway, the Via Maris (Artzy and Marcus 1991, in press).

The observation that MB IIA settlements existed along all the coastal river basins and at the outlet of nearly each river supports the theory that coastal river mouths, estuaries or inland bodies of water fed by these rivers served as natural anchorages for ships. A coastal forward port settlement would be located near the anchorage and an inland site further upriver would provide communication with the agricultural hinterland. This hypothesis is predicated on paleogeographical reconstructions of the shoreline since nearly all these waterways are currently inaccessible to navigation (Raban 1985:11-23, 1980:750-54).

The MB IIA period at Tel Nami is represented in Areas D, G and O. In Area D, located on the eastern most part of the tell, finds easily datable to this period were discovered (Artzy and Marcus 1991, in press). During this period, the area was used

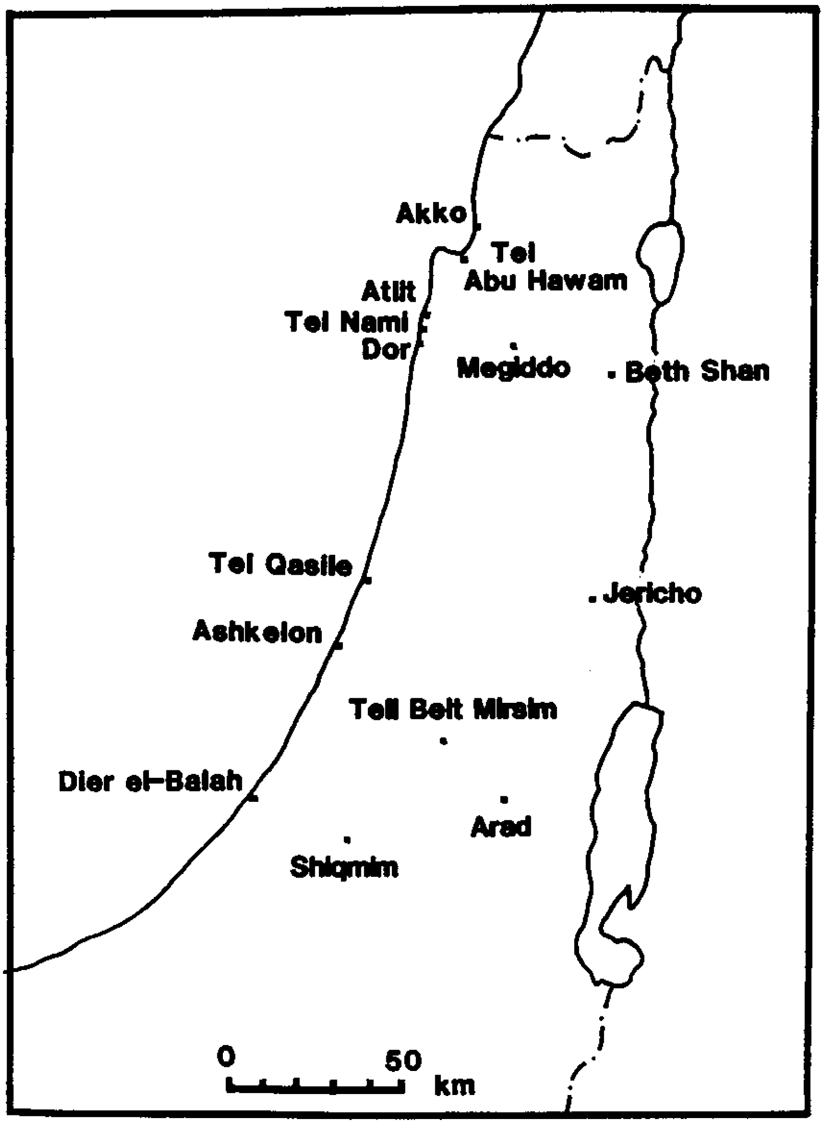


Figure 4. Map of prehistoric settlement in Israel.

for storerooms, probably connected to the anchorage (Artzy 1990:76). The discovery of charcoal, ash and burnt mudbrick indicates that the storeroom was destroyed by fire. Over 25 vessels have been found in Area D, including storage jars, kraters, bowls, juglets and a pithos. Many of the jars were found with their contents in situ. The organic remains included seeds of wheat, chick peas, grapes and an exotic legume apparently imported from the Aegean (Kislev, Artzy and Marcus 1991, in press). A terra cotta scarab-sealed weight was also found. Preliminary analysis indicates that the seal belonged to the reign of Amenemhet III who reigned ca. 1842-1797 (or 1859-1814), when Egypt had strong contacts with Byblos and northwestern Syria (Artzy and Marcus 1991, in press).

In Area G, the uppermost part of the tell, remains of the MB IIA period are found almost two meters down from the surface. One of the most interesting finds among them is a drainage system that was found in situ. Street levels have been excavated, and there are MB IIA walls. Artifacts include pottery sherds dating to the period, and a small bronze arrowhead. An MB IIA phase may be evident in Area O, located across the tell at Nami East, in the form of stone walls and a cistern.

The Late Bronze period is also well-represented at Tel Nami, separated by a 70 cm layer of sterile windblown sand from the remains of the Middle Bronze IIA. As with the end of the Middle Bronze Age IIA at Tel Nami, there is also strong evidence for a violent destruction at the end of the Late Bronze IIB period in the form of burnt materials and ash.

Two areas that reflect the international flavor of this site during the Late

Bronze Age are G, D1 and O. Stone walls, crushed mudbrick, bronze objects, jewelry, and imported pottery characterize Area G for this period. Much of this material is associated with a LB IIB temple. It appears, however, that a Late Bronze IIA settlement preceded the LB IIB phase, and was destroyed by fire. In several squares in Area G, a robbed floor of the LB IIA stratum was discovered. The ruins of the LB IIA phase were then used to construct the foundation for the rampart of the LB IIB period. The rampart fill contains the foundations of earlier walls, ruins of buildings, mudbricks and ash, as well as sand from other parts of the site (Artzy 1990:75). The predominant and remaining occupation in Area G is datable to the Late Bronze IIB.

Area D1, which is located right above Area D, consists of LB IIB stone floors, foundations and fallen mudbrick. Numerous pieces of bronze, possibly scrap metal were found in this area.

The Late Bronze period in Area O superimposes the structures of the MB IIA not far below it, and the inhabitants of the LB IIB phase borrowed stones from these structures to build their cemetery. The graves, buried underneath the sand dunes of Nami East, are of different types: stone-lined elliptical graves, rectangular pit, graves and one complete burial in a collar rim pithos, sealed by a Canaanite storage jar (Artzy 1990:76). Although most graves were robbed in antiquity, some were missed, and Area O has yielded some significant finds which parallel those of the Ulu Burun shipwreck (Pulak 1988: 1-37). These include a pilgrim flask, oil lamps, and imported Mycenaean and Cypriot wares, including fine-ware vessels of White Slip II ware, Cypriot "Milk Bowls," Base-Ring II and White-Shaved juglets. Jewelry has also been found, including Egyptian scarab rings and other pieces possibly of Aegean origin or influence.

The occupation of the tell and Nami East ends with the Late Bronze Age IIB. Some Byzantine pottery has been found on the tell, but not enough to substantiate any real occupation. The only other indication of human activity is in the form of twentieth-century military testing. The site now remains covered in sand and dirt when not being excavated.

The Coastline

The available archaeological evidence combined with geologic data indicates that during the Bronze Age, tectonic forces and fluctuating sea levels affected coastal morphology. Due to a combination of these factors, a large number of swamps developed along the lower parts of the coastal plain where dunes and kurkar ridges acted as barriers, catching flood waters (Nir 1982:89), possibly providing anchorage for maritime traders (Flemming et al. 1978:37).

At Tel Nami, the presence of reeds and other hydophytes around the fish ponds at Nami East indicate that the area was once a natural swamp or brackish lake fed by Nahal Me'arot (cave river). The Nahal Me'arot, like other rivers that drain into the Mediterranean, is a small and ephemeral (Nir 1982:89) river that originates in the Carmel mountain range. It now lacks a distinct outlet since the water is diverted to irrigate the fish ponds.

Geomorphological investigations and cartographic evidence dating as far back as 1799, tend to support the notion that the Nahal Me'arot changed its course over the millennia, and that at some time coinciding with periods of habitation at the site, it emptied out into the sea near the vicinity of the tell (Artzy and Marcus 1991, in press). The lake that was fed by the Nahal Me'arot may have served as a protected anchorage for maritime coastal traffic since boats could gain access to the lake through the stream's estuary which ran between the tell and Nami East (Artzy 1986:16). Because Israel's coastline lacks any natural harbors with the exception of Haifa Bay and the associated projection of Mount Carmel (Horowitz 1979:12) (Figure 5), utilizing small river mouths as inner anchorages would have been a viable solution (Artzy 1991, in press).

A genetic classification that applies to the Israeli coastline is C.A. Cotton's "coasts of mobile regions" (Cotton 1952:315). Cotton's classification system divides coasts into either stable or mobile regions. Israel's coastline fits the latter description since it has been affected by Holocene tectonic uplift and submergence, along with faulting and folding. Changes in coastal morphology due to tectonic activity was probably partly responsible for the shift of the Nahal Me'arot as well, since much of the morphology and shape of Israel's coastline can be attributed to plate tectonics and active faulting (Neev et al. 1987:ix).

Along with tectonic activity, it is generally agreed that changes in sea level have occurred, but there is disagreement concerning rates and changes. Much of the evidence for a rise in sea level along Israel's coast comes from investigating coastal archaeological sites. Relative changes in sea level at archaeological sites are noted in

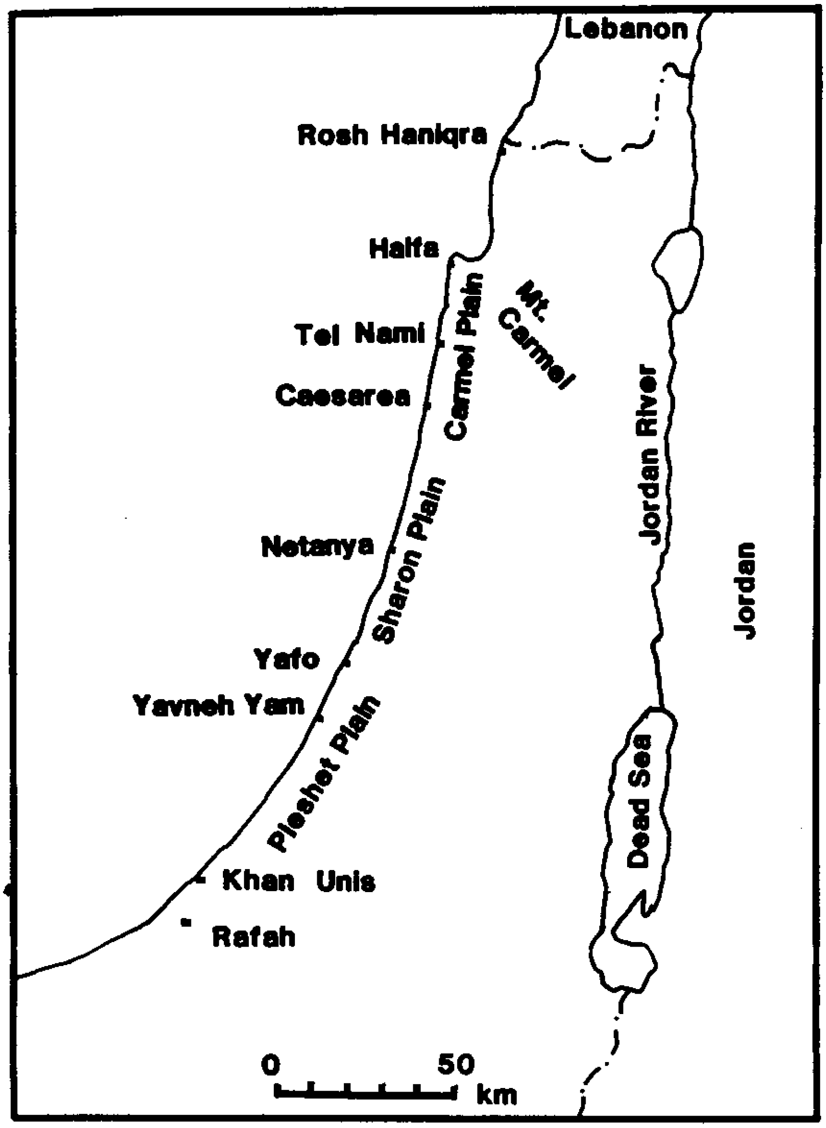


Figure 5. Map of Israel's coastline (after Nir 1985:506).

submerged or partially submerged structures since they were built in precise relation to the level of the sea at their time of use (Flemming et al. 1978:37).

A closer examination reveals that eustatic changes, changes that affect the volume of sea water, have varied locally, depending on climatic and regional conditions (Pirazzoli 1987:175). Isostatic changes in sea level, changes dependent on tectonic activity, have also taken place. The two types of changes in sea level often act together, producing a complex result (King 1972:192).

The position of the tell and the settlement patterns for the successive occupations at Tel Nami reflect the coping strategies of the inhabitants to the rising sea level during the Bronze Age. For example, in Area D, there are signs that the occupation of the MB II period extended further south and south-east than that of the Late Bronze Age. The change in sea level in the LB IIA reduced the area of settlement. During the LB IIB phase, the living area shrank even further (Artzy 1990:76).

The conditions resulting from sea level changes and tectonic activity along Israel's coast include the formation of estuaries. According to Nichols and Biggs (1985:84), estuaries develop along low-lying coasts that are subject to tectonic activity. Estuaries also develop along sandy coasts where longshore currents carry sand, creating spits or barriers across river mouths (Figure 6). The sandy, low-lying coastline where Tel Nami is located fits the above description.

Eventually, estuaries fill up with fluvial and marine sediments. Enclosures by spits and barriers will also accelerate the infilling of an estuary. Because the

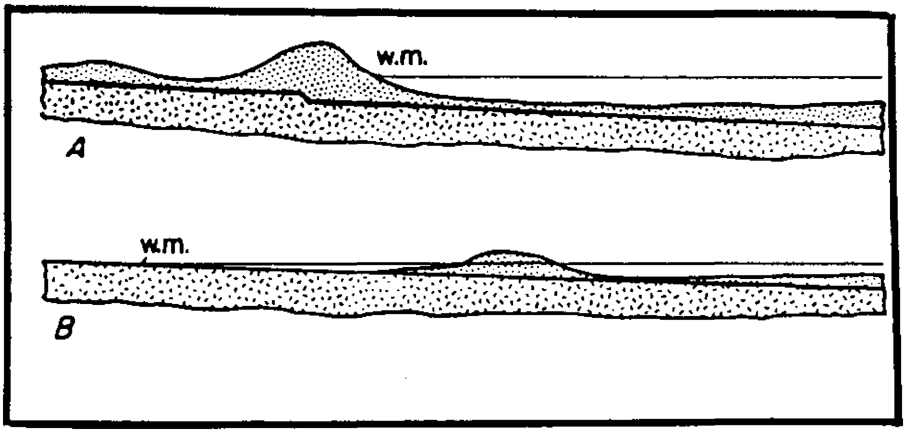


Figure 6. Coastal profile types for Israel: (A) Sand-ridge coast and (B) Bar-and-lagoon coast (w.m. = water mark) (from Butzer 1971:220)

Mediterranean lacks a tide, ancient harbors filled up with sedimentation (Raban 1988:200). Galili (1986:71-72) doubts that gently graded beaches like Tel Nami would have adequately provided navigable estuaries and natural harbors for ancient mariners since the waterways would have filled too quickly with sediment and sand. Thus, maintaining a navigable stream would have required a continuous dredging of sand, an impracticable task during antiquity. Galili, however, overlooks the aspect of the flushing velocity of the Me'arot during the Middle and Late Bronze Age, which could have been adequate enough to slow-down sedimentary build-up. Climatic changes also could have resulted in exceptional hydrodynamic conditions that would have pushed river sediments seaward, so that natural estuaries and harbors did not fill up as quickly as Galili claims.

In conclusion, while sedimentation no doubt occurred, the equation of river-coast anchorages along the Syro-Palestinian coast remained viable enough to maintain settlements and trade contacts throughout the Middle and Late Bronze Age. That Tel Nami served as an anchorage during this period is partially evident through the discovery of imported goods. Found among these were a number of bronze objects. By the Late Bronze Age copper and bronze were valuable commodities that were traded in bulk in the form of ingots, or as scrap metal and objects of utilitarian and cultic use. This variety represents a technological achievement that evolves from many centuries of experimentation and refinement. This evolution in copper metallurgy is examined in more detail in the next chapter.

CHAPTER II

THE EVOLUTION OF COPPER METALLURGY IN THE EASTERN MEDITERRANEAN AND NEAR EAST

Introduction

While articles made of copper and copper alloys have been in use for several thousand years, the archaeological evidence for copper metallurgy in the ancient Near East and Eastern Mediterranean is fragmentary. It is generally agreed that copper metallurgy began with the use of native copper to make small items such as awls or pins.

The earliest evidence for the use of copper comes from Shanidar Cave in Iraq, in the form of a small oval pendant, dated to the early ninth millennium B.C. (Solecki 1969:311), although the pendent is now believed to be malachite rather than metallic copper (Solecki, personnel communication 1991). Artifacts made from native copper have been recovered from Level IX at Çatal Hüyük, in Turkey, dating to the seventh millennium B.C. (Mellaart 1964:111).

Ores and Mining

Copper is distributed world-wide in its native malleable state or in a variety of mineral ores (Healy 1978:57). Native copper only occurs in limited quantities in the oxidation zone of a copper deposit, and assumes different morphologies. The largest block of native copper ever reported came from Minnesota in 1856, weighing about 500 tons (Alexander and Street 1976:25). Native copper also occurs in smaller, more manageable lumps or as branches in rock faults

Copper mineral ores are more common than native copper, occurring in the zone of secondary enrichment. This zone can be divided into two further zones: the upper, oxidized zone above the water table where carbonates, oxides and pure minerals are deposited, and the second zone below the water table as the zone of sulphide enrichment (Kirkaldy 1970:94) (Figure 7). The oxidized zone is characterized by copper oxide, cuprite, and the copper carbonates, malachite and azurite. These minerals appear as blue or green veins in the surface breaks of contact metamorphic zones or in weathered outcrops known as gossans (Wertime 1973:878). Below the water table, the unweathered parent ore forms the zone of sulphide ores, chalcolite, covellite and the chalcopyrites (Hodges 1976:65).

Remains for ancient copper mining in the Near East and Eastern Mediterranean are scarce or difficult to interpret. To explain the lack of archaeological evidence for ancient mines, de Jesus (1980:99) suggests that mining occurred in isolated, mountainous areas, and possibly as a seasonal activity, far from settlement sites. These mining sites are overlooked or destroyed by weathering and seismic activity. Ancient mining operations are especially hard to identify and date because any subsequent disturbances or continuous mining could obliterate traces of previous workings (Weisgerber 1982:27).

Early evidence for actual copper mining comes from the shaft mines of Rudna Glava in Serbia (Jovanović 1988:70) and at Ai Bunar in southern Bulgaria (Jovanović and Ottaway 1976:106-107) (Figure 8). At Rudna Glava, where 40 shafts were

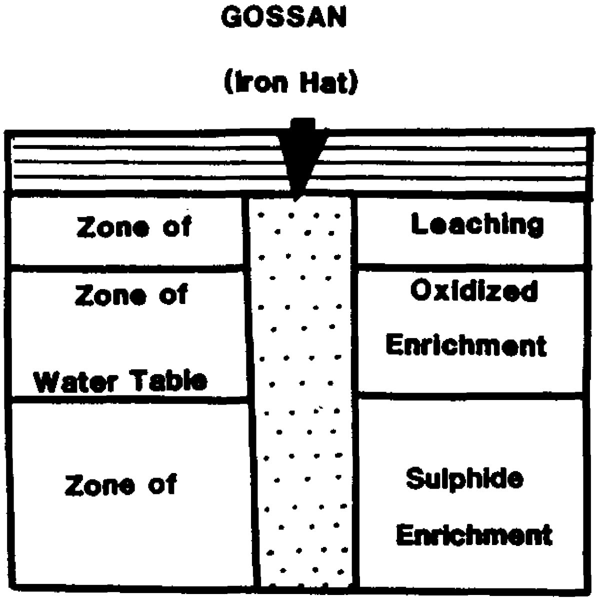


Figure 7. Zone of secondary enrichment (after Kirkaldy 1970:94).

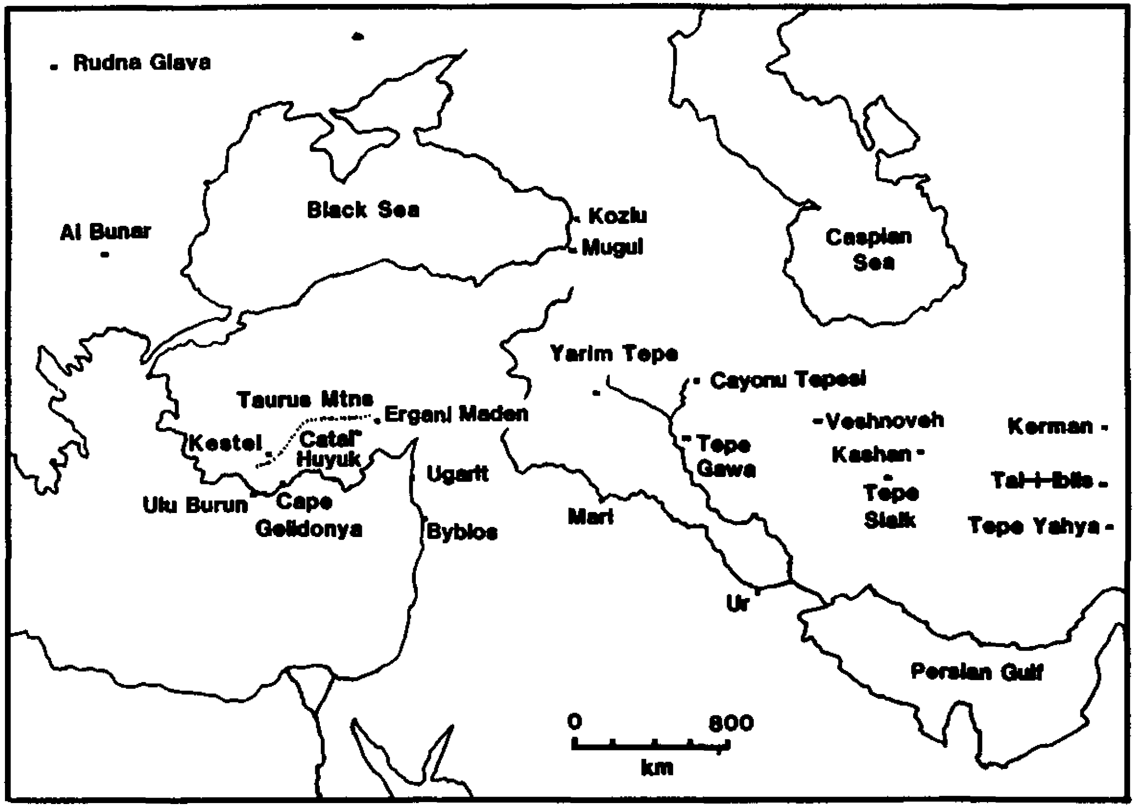


Figure 8. Map of settlement and mining sites mentioned in the text.

discovered, it appears that the ore mined was chalcopyrite. Mining activities at this site date to the second half of the fourth millennium B.C. (Jovanović 1988:73).

At Eneolithic Ai Bunar, mining shafts and access platforms were discovered. The ores were probably removed by use of bone and wooden wedges and pulled to the surface. The shafts followed the configuration of the ore veins, which mostly consisted of malachite and some chalcopyrite (Jovanović and Ottaway 1976:107).

Evidence of any activity has been recovered on the Sinai peninsula and the Eastern Desert (Figure 9). Numerous copper and turquoise mines and smelting centers have been located in the Timna Valley in the southern Sinai desert. The mines are scattered throughout the southern plateau, an isolated hilltop with rocky slopes. The mines date from the Chalcolithic Period through the mid-twelfth century B.C. (Rothenberg 1988:8), although Muhly (1973:219) and others propose that Egypt's main source for copper from the Middle Kingdom onward was Cyprus.

Because Timna is one of the few surviving sites of discernable mining activity, it is often cited as an example of the progressive technological developments in mining and metallurgy technology in the ancient Near East. The progression begins with open cast mining, which consists of cave-like entrances that lead to the side of an ore deposit.

The earliest Chalcolithic mines at Timna have been identified by artificial round cave-like entrances, particularly Site 42, an outcrop containing copper ore nodules (Rothenberg 1972:27). Open cast mines dating to the Ramesside Period of the New Kingdom have been found in association with a variety of stone tools

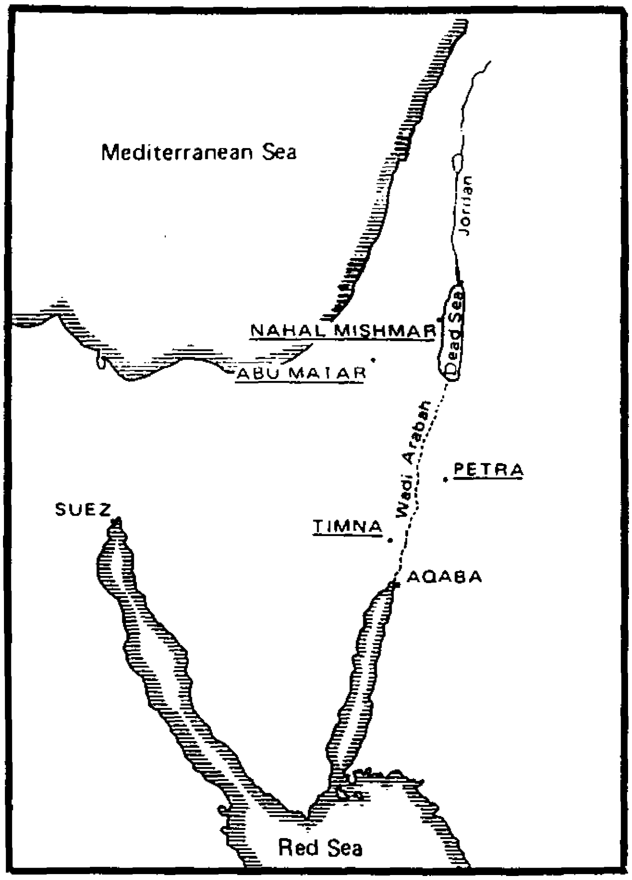


Figure 9. Map of southern Israel and Sinai (after Weisgerber and Hauptmann 1988:53).

(Rothenberg 1972:63), along with tunneling, observed by Erman (1971:468-9) at Wadi Maghara and Wadi Nasb in the Sinai peninsula.

At the end of the fourteenth century B.C., according to Rothenberg (1988:11), an Egyptian mining expedition set up sophisticated shaft and gallery operations. Most of these shafts are horizontal and follow the veins some 40 to 50 m into the rock (Bromehead 1954:564). The techniques used were similar to those used in quarrying the rock-cut tombs in Upper Egypt. The rock was chiseled with a copper or bronze spike that was pounded by a wooden mallet to break the ore, or else a wooden-handled bronze hoe was wielded like a modern pick-axe (Bierbrier 1982:46).

While Timna may serve as a valuable source for understanding ancient Near Eastern mining technology, its technological developments may have been entirely local in nature, and unusual in the Levant (de Jesus 1980:116).

Another useful guide in identifying ancient mining activity is the presence of mining tools. According to de Jesus (1980:105-108), mining tools comprised wooden, stone and metal implements. Wooden tools, of what survives, include shovels, hammers, picks and battering rams. A wooden shovel from the Murgul copper mine in Anatolia, has been dated to the late first millennium B.C. (Kaptan 1977:96).

Basalt was an ideal tool for picks and gads (wedges). Stone was also used for hammers, mortars and pestles. Stone mining tools have been discovered in tomb and settlement contexts on Crete, dating to the Early and Middle Bronze periods. They include axe-hammers with broad, sharp blades and blunt ends, and various hammers with shafts. These tool were probably used to break off lumps of mineral ore (Branigan 1974:66).

Metal tools for mining have been found out of context, and their multiple use makes it difficult to identify them as specifically for mining (de Jesus 1980:106). Metal tools for mining include adze-hammers, axe adzes, flat axes, chisels, picks and axe-hammers. Three double bronze axes, slightly splayed, were found at Ghardiki in Greece, possibly dating to the Late Bronze Age (Davies 1935:242).

Another indication of mining activity is the relationship of settlement sites in close proximity to potential mining areas. Over 50 metallic hammered copper artifacts have been found at the Neolithic site of Cayönü Tepesi in southeastern Turkey, dating to ca. 7250-6750 B.C. (Braidwood et al.1981:250, Çambel and Braidwood 1983:157). The nearby Ergani Maden mines, located about 20 km north of the site, may be the source for the native copper objects found at Cayönü Tepesi and other Neolithic sites in Anatolia and northern Mesopotamia (Muhly 1988b:6). There is some doubt as to whether native copper was abundant at Ergani Maden (Birgi 1950-1951:340). With modern mining activity in the area, much of the archaeological evidence to verify this has been obliterated (de Jesus 1980:109).

In 1973, a team of geologists discovered an ancient copper mine at Kozlu in northern Anatolia. The site dates to 2800 B.C., based on carbonized wood samples taken from the shaft poles. It is composed of an outcropping of secondary ores from the oxidized zone, and a sulphide layer extending along the mineral horizon at the surface. No tools were found, but a shaft and gallery indicate that the area was mainly exploited for its copper sulphide ores (Giles and Kuijpers 1974:823-825).

At present, no dated copper mines have been located for southern Mesopotamia, although in an inscription found at Ur III, the ruler Gudea mentions copper from the mountains of Kimas, which are part of the Kerman Range (Figure 8). This is a possible source for ancient Sumer (Limet 1960:110). Holzer and Momenzadeh (1971:5) describe copper mines in the Veshnoveh area in west central Iran at Mazrayeh and at Chale Ghar. At Mazrayeh, cave-like diggings with rounded entrances were exposed, while at Chale Ghar, two to three narrow tunnels lead to a network of small holes, short inclines and narrow stopes. An unglazed vessel found at Chale Ghar dates the site to the early fourth millennium B.C. (Shepherd 1980:193). Caldwell (1966:4-5) reports that there are copper ores in the Kerman Range in southeastern Iran, a possible source for ancient southern Mesopotamia.

In recent years, a provenancing technique known as lead isotope analysis has shown some promise in locating the original source areas for copper (Reedy and Reedy 1988:65). This involves a statistical sampling to quantitatively determine a metal's origins (Sayre 1988:41), and is based on the premise that lead deposits were formed at different geologic episodes or under varying geochemical conditions which serve as isotopic fingerprints in the geologic record. Specific isotopic compositions are composed of the four stable isotopes of lead: Pb^{204}, Pb^{206}, Pb^{207} and Pb^{208}. These isotopic compositions can be matched with ores of known mining regions (Brill et al. 1973:73).

The advantages to using this technique are twofold; it only requires a small sample, causing less damage to an artifact, and the chemical history of an object does not interfere with the isotopic reading (Brill et al. 1973:73). Lead isotope analysis has been used for pigment studies (Keisch and Callahan 1976:181-193), and for provenancing silver in archaic Greek coins (Muhly 1988a:338). The most active adherents of lead isotope analysis are Noel Gale and Zophie Stös-Gale of Oxford University.

There are some inherent problems in using this technique. While a given lead deposit has its isotopic ratios, the ratios are not always unique to that deposit. Isotopic compositions of lead from separate sources may be indistinguishable if the deposits were formed under similar geologic conditions (Healy 1978:220).

Another drawback to this method is the problem of metal salvaging and remelting of scrap metals together. This results in an inaccurate isotope reading where the reading reflects a midpoint between the ratios of the original metal and those added to the mix (Brill et al. 1973:73). Yet the Gales claim that scrap metal was only hoarded and traded in any quantity at the very end of the Late Bronze Age (Gale and Stös-Gale 1985:90), so that lead isotope analysis is reliable up to this point.

The Development of Smelting Technology

Attempts have been made to reconstruct a technological sequence of developments for ancient copper metallurgy technology (Renfrew 1979:171-173). Some of these reconstructions have been based on diffusionist theories that attribute the spread of metallurgy technology through the exchange of ideas. Childe (1944:17) maintained that copper metallurgy technology originated in the Near East, then spread out to the Aegean, the Balkans and central Europe. In a similar vein, Wertime (1973:885-886) maintains that copper metallurgy began in the upland belt and river valleys of southwestern Asia and spread from there.

Recent trends, however, favor separate regional developments as Reed first suggested in 1934 (383). For example, Davey (1988:68) proposes that the metallurgical tradition of Mesopotamia, northern Syria, Palestine and Egypt, which he designates as the "Southern Tradition," differs from the traditions of Iran, Anatolia and areas of the Mediterranean.

Tracing a logical sequence of developments in copper metallurgy is hampered by the poor preservation of metal artifacts, the random nature of archaeological discovery and chronology problems (Muhly 1988b:2). Another problem is the confusion over terminology. Melting and smelting are loosely used terms that have been interchanged since they both involve molten metal, but their meanings are definite and distinct. Melting refers to the physical conversion of a solid to a liquid, whereas smelting is a chemical change where a mineral substance converts to a metal.

The confusion is also partially based on the examination of crucible slag remains. In analyzing these fragments, there is often disagreement over whether the operation was one of smelting or simple melting. Tylecote (1976:5) argues that crucible slags of native melted copper can be distinguished from smelted copper ores. Unlike melted native copper, smelted copper contains small amounts of ferrous silicates from the iron oxides used in fluxing.

Wertime (1968:935) believes that crucibles were used only for smelting rather than melting, although melting copper in a crucible may have led to the development of smelting technology. Madden et al. (1980:223) conclude that no adequate criteria exist to distinguish melted native copper from worked and recrystallized smelted copper of high purity. Under microscopic examination, both reveal similar deformations. Rapp (1988:23), however, states that a detailed chemical analysis will lead to the distinction. A chunk of slag recovered from Level VI A at Çatal Hüyük is still under question. Tylecote (1976:5) dismisses this as slag, while Cooke and Nielson (1978:182) view it as purely representative of melting, if it is slag at all.

In tracing the development of copper metallurgy, several theories have been proposed over the years. The most popular and enduring is the "camp fire" scenario which depicts prehistoric ancestors unwittingly building a hearth with copper bearing ores. A hot fire, stoked by wind, would leave blobs of metallic copper in the ash heaps. This basic outline has been reconstructed and embellished to produce romantic accounts such as the one below (Davis 1924:24):

> That night, the thoughtful chief dreamed of rivers of reddish, fiery liquid sweeping over and annihilating his enemies. Before the sun rose, he was raking over the ashes of the festal fire of the night before. No liquid was there. But he found a strange stone, blackened and shaped like a frozen puddle. He wondered at it, and tried to crack it with a stone quarry sledge. It did not split asunder, but the blow left a dent, a mark that was like that left on the valuable reddish rock of the quarry that was so much desired.

The application of heat to stones was already a part of flint technology (Charles 1979:8), so this scenario was unlikely. Also, the melting point of copper requires high heat, up to 1083°C, which is rarely possible in an open camp fire, even under windy conditions. For copper to be melted or smelted, two conditions must be met. First, the necessary high heat, and secondly, an oxygen-starved atmosphere rich in carbon. These conditions draw oxygen from the heated ore and reduce copper to a molten, metallic form (Coghlan 1975:28).

When native copper is melted, the unwanted portions of the ore, called gangue, separate out from the molten copper. These soluble segregates dissolve, leaving a homogenous metal (Tylecote 1976:2). Any residual gangue left forms a lighter molten substance which hardens and becomes a glassy substance called slag (Raymond 1984:10-13). While an open campfire made with charcoal produces carbon monoxide to act as a reducing agent, Coghlan (1941:57-60) found that the proper reducing conditions were lacking in his experiments with simulated campfires.

Since the 1970s, other theories have been proposed to explain how copper metallurgy began. Charles (1979:9) maintains that smelting and melting were not separate innovative events. Rather, native copper would be melted along with its associated oxide minerals. During heating the ores were recognized by their distinctive colors and odors. As native copper became scarce, closer attention would have been paid to the mineral ores (Charles 1979:9, 1980:163).

Wertime (1973:882) suggests a similar development, whereby early smelting involved reducing several metallic ores in juxtaposition with one serving to flux the others. Wheeler et al. (1979:16-17) also propose that smelting and melting were contemporaneous. Coghlan (1975:29), on the other hand, views this as unlikely for it would depend on the native copper being associated with adhering minerals of a suitable nature. Therefore, in his view, melting preceded smelting in metallurgical development. The chief difference that distinguishes melting from smelting is the separation of the molten reduced copper from the gangue by the use of a flux. Charles (1979:9) proposes that iron oxides served as the first flux material, since they occur naturally as part of a gossan deposit.

To create the high temperatures needed to smelt copper requires a closed container that can provide the proper reducing conditions. Hodges (1970:65) suggests that in fourth millennium Mesopotamia, the method for making faience, (Egyptian type) was adapted to smelting metal. The faience was made from sand with soda or potash added to form a quartz paste, which was then fired at high temperatures in a closed container, much like a crucible.

Coghlan (1975:30) suggests that the prototype for the Bronze Age smelting furnace was the pottery kiln. Experimenting with a small kiln-like chamber and charcoal, he was able to produce small beads of copper from crushed malachite (1941:60-63). Potters were well-versed in maintaining the necessary conditions for firing. The evidence from Çatal Hüyük supports this hypothesis by the production of black and red pots made from the same clay (Raymond 1984:13-14). In a kiln, malachite can reduce to metallic copper given the proper reducing conditions. Both malachite and azurite will decompose below a temperature of 200°C, according to experiments conducted by Simpson et al. (1964:1114), so that early copper smelting could have been conducted below the melting temperature of copper (Caldwell 1966:12).

From his archaeological report on the Neolithic site of Tepe Sialk in Iran, Ghirshman (1938:38-39) describes a type of kiln that could be applicable to developing furnace technology. Inside the kiln, a fire would be lit underneath the chamber with a shelf above it to hold the pottery. Mylonas (1929:16.) reports a similar type from his excavations at Olynthos (Figure 10).

Whether or not the Neolithic pottery kiln was the precursor to later smelting furnaces, it appears that furnace technology evolved from a simple operation. According to Tylecote (1980:183), a pottery kiln itself would not be suitable for smelting since the chemical transformation of converting an ore to metal is different than the process of hardening pottery. In order to reach the necessary reducing conditions to cause separation of metal and ore, close contact between the ore and charcoal is necessary. This does not follow pottery kiln design. Rather, the reduction process is best carried out in a clay bowl or hole in the ground where the right proportions of charcoal to ore are combined. A typical Chalcolithic furnace then would consist of a bowl-shaped depression in the ground with a pile of hot charcoal and stones. The fuel and ore were piled together in the depression, with the addition of forced draught (Figure 11). During smelting, the slag and metal would form simultaneously and separation would take place in the lower part of the furnace since slag has a specific gravity of 3.5 to 4.0 while metal is about 8.9.

To complete separation between the slag and copper takes time, so the Chalcolithic smelter would have settled for a mixture of copper and slag, which he could then break up into pieces once it cooled. In breaking up the pieces, the smelter could recover small globules of copper known as prills, trapped inside (Tylecote

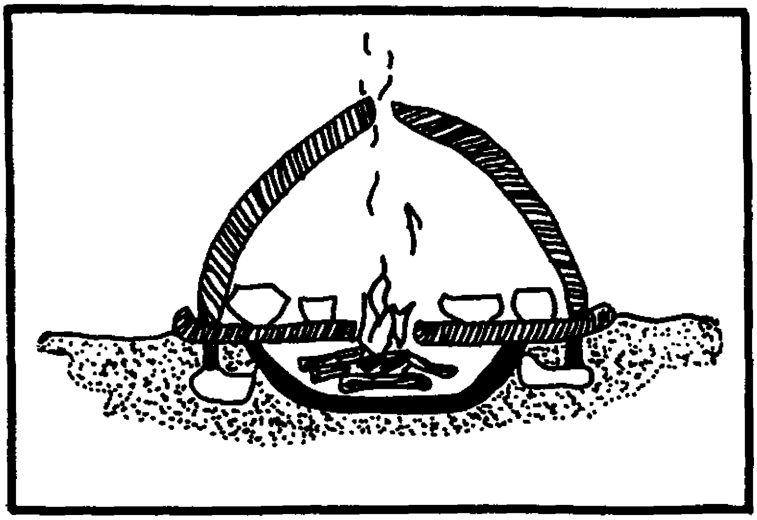


Figure 10. Early pottery kiln prototype for copper smelting furnace (after Mylonas 1929:310).

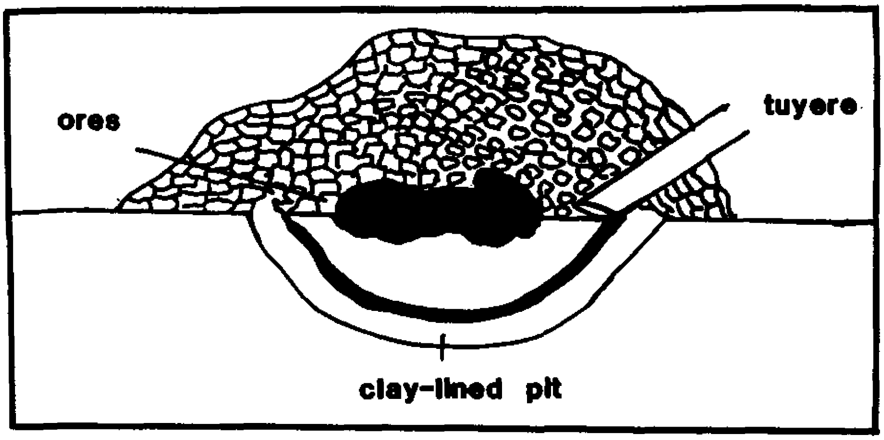


Figure 11. Early type of copper smelting furnace with bowl-shaped depression (after Tylecote 1976:18).

1980:185, Rothenberg 1985:124). The copper prills were then refined by placing them in a crucible in the furnace.

Based on his findings from Timna, Rothenberg calculates a Chalcolithic furnace to be about 20 cm in diameter and 40 to 50 cm in height, which includes a superstructure of stone. A similar furnace type was discovered by Glueck (1940:59, 63) at Khirbet-Jariyeh and Khirbet-en-Nahas in the Wadi Arabah (Figure 12). Although these are Iron Age sites, their furnaces vary little from the type proposed by Rothenberg. Khirbet Nahas was a copper mining and smelting site. A number of smelting furnaces, copper slag and ruins have been found there. Less than 3 km from Khirbet Nahas is Khirbet Jariyeh, where two types of smelting furnaces were found, the square type similar to the type found at Khirbet Nahas, measuring 2.70 m, and a rounded version, approximately 2.9 by 2.6 m, as described by Glueck (1940:63).

Limet (1960:114-115) mentions a rounded type of furnace with a chimney to release fumes, which he partly bases on the Assyrian sign GIR (Figure 13), which he claims visually represents an image of a smelting furnace. A copper smelting furnace from the tenth century B.C., Level XI at Tel Qasile near Tel Aviv provides an example of this design (Figure 14) (Maisler 1950-1951:74, Mazar 1985:127).

Charcoal was the chosen fuel from the Chalcolithic period onward, because it could provide the necessary high heat. Properly carbonized charcoal contains little or no hydrogen, thus eliminating gas bubbles which can spoil a casting (Tylecote 1962:109). Efficient and controlled smelting also required the use of forced draught

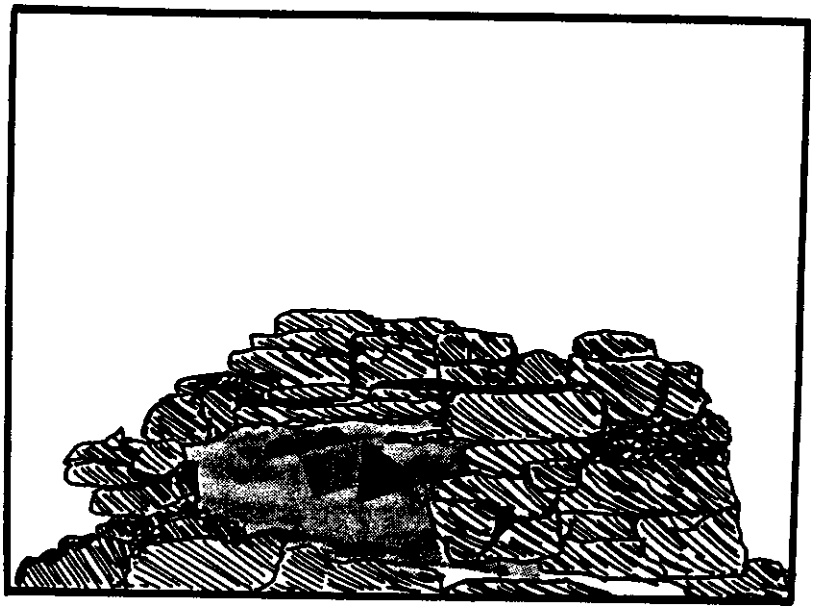


Figure 12. Copper smelting furnace from Khirbet Jariyeh (after Glueck 1940:63).

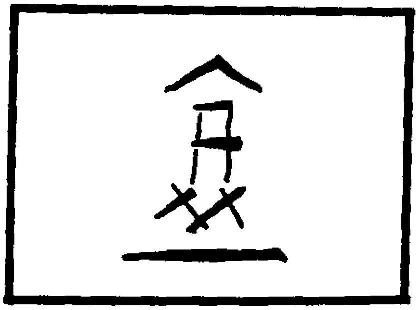


Figure 13. Assyrian sign GIR representing a copper smelting furnace (Limet 1960:114).

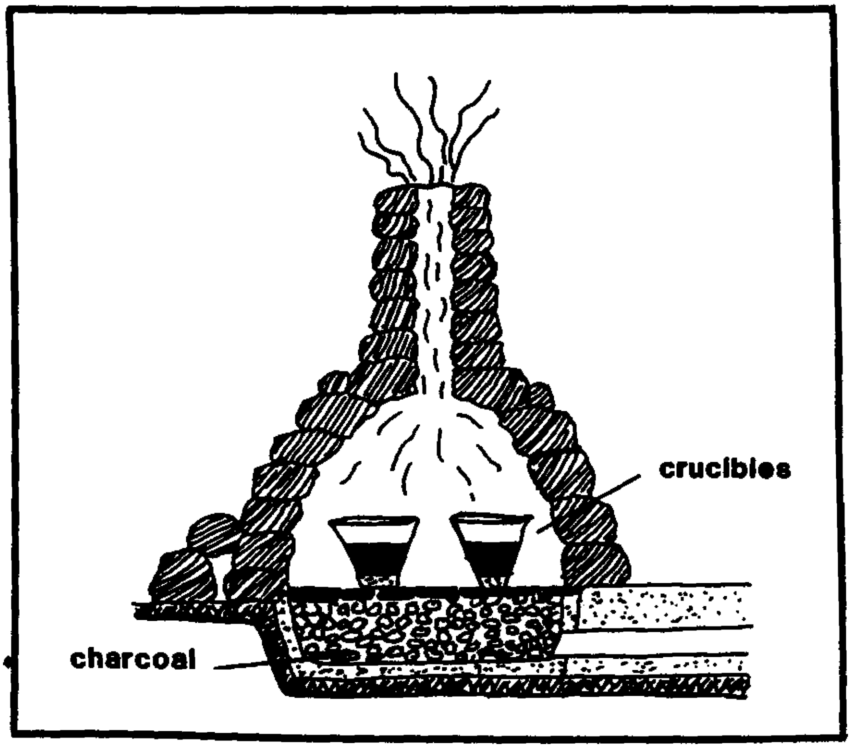


Figure 14. Copper smelting furnace from Tell Qasile (after Maisler 1950-1951:74).

to the furnace, which was provided by clay blow pipes, as seen in the Egyptian tomb of Hepu at Thebes (Figure 15). Blowpipes were still used in the Late Bronze Age, but probably for welding and soldering (Zwicker et al. 1985:104).

By the Late Bronze Age, clay tuyeres were used to provide forced draught. They were extended into the furnace horizontally or vertically with bellows attached at the other end of the tuyere. A blast of air was provided by pumping the bellows. A similar arrangement is depicted in the Eighteenth Dynasty tomb painting of Rekhmire, where Egyptian metalworkers are shown smelting, melting and pouring casts to make bronze doors (Figure 16). This type of arrangement has also been observed in different parts of Africa in the twentieth century (Hodges 1970:142, Bernus and Echard 1985:75).

Bellows were introduced to Egypt by the Hyksos in the first quarter of the second millennium B.C. (Zwicker et al. 1985:104), and could be operated by hand or foot. Hand-operated bellows have been found in Anatolia, the coast of the Levant and Cyprus, while the foot-operated bellows have been discovered in Mesopotamia, the inland areas of the Levant, Sinai and Egypt (Davey 1988:66). One type of bellows known to have been used were the pot bellows. Cumbersome and large, pot bellows were probably used in large-scale smelting operations, while more portable small skin bellows were used in smelting operations near the mines (Davey 1979:110-111).

It is conceivable that smelting was done as early as the sixth millennium B.C. The recovery of a necklace of 13 lead beads from Level VIA at Çatal Hüyük

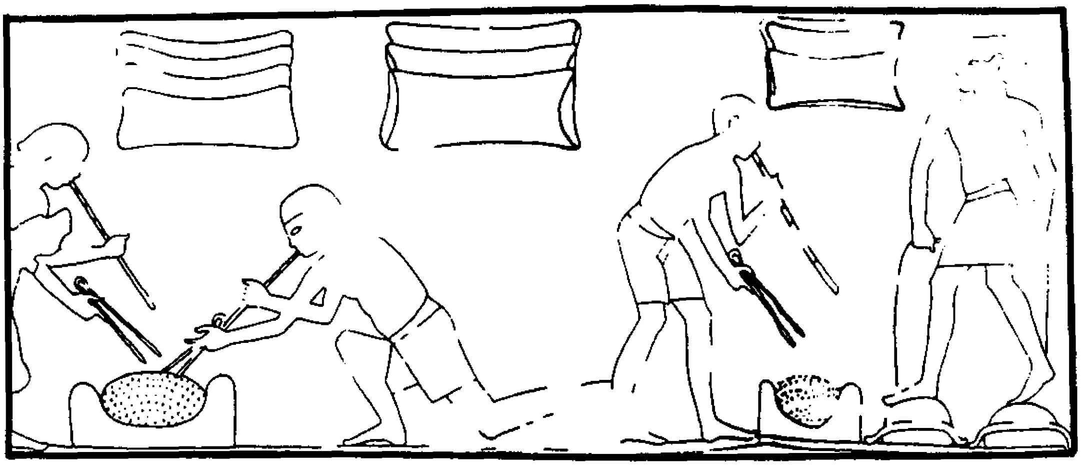


Figure 15. Blowpipes being used in the smelting process. From the tomb of Hepu at Thebes (from Garis Davies 1963: Plate VIII: by permission of Oxford University Press).

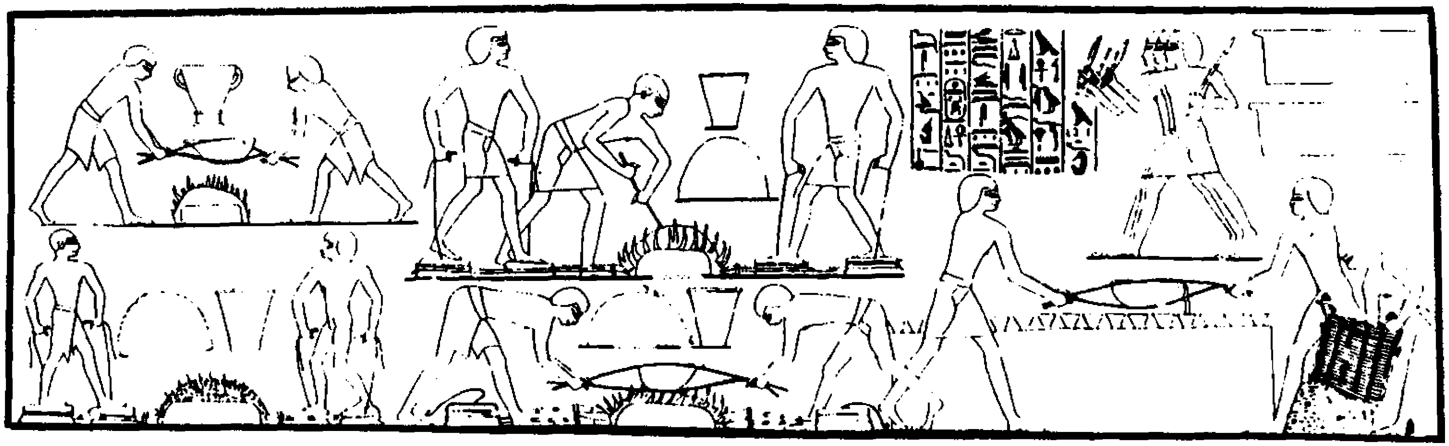


Figure 16. The smelting melting and casting of bronze as depicted from the tomb of Rekhmire (from Garis Davis 1973: Plate LII).

(Mellaart 1967:217) and a lead bracelet from Yarim Tepe I in Level XII, (Merpert et al. 1977:82) is significant. Lead does not occur in a native state as copper does, so it must be obtained from ores (Wheeler et al. 1979:17), usually galena. Lead ores can be smelted in a wood-fueled fire, since the separation of lead as molten metal requires only temperatures in excess of 327°C (Charles 1985:22).

While the presence of lead this early in the archaeological record indicates a knowledge of smelting technology, no concrete evidence exists for smelted copper prior to the fifth millennium B.C. (Muhly 1988b:7). The earliest example of smelted copper artifacts comes from Tepe Yahya in Iran, dating to the late fourth millennium B.C. (Tylecote 1976:5).

Alloying: Arsenic

The first clear evidence for alloying copper in the Near East and Eastern Mediterranean comes from objects that have a high arsenic content. Copper-arsenic alloys first date to the end of the Chalcolithic Period and precede the use of tin-bronzes, which appear in the Middle Bronze Age (Charles 1985:25). Copper-arsenic alloys become the dominant form of copper metallurgy in the third millennium B.C., in the Levant, Aegean, Anatolia, Egypt, Transcaucasus and Central Asia (Muhly 1977b:74-75, Eaton and McKerrell 1976:174).

The use of arsenical copper also supports the hypothesis that copper metallurgy developed according to copper deposit stratigraphy (Tylecote 1976:8), whereby the oxidized ores in the weathered surface outcrops were utilized first, followed by use of the deeper sulphide ores. (Charles 1985:23). Arsenical copper minerals are often found in association with other minerals in a copper deposit, in the oxidized zone as green arsenates similar to malachite in appearance (Charles 1979:10). Arsenates also appear in veins of lead, silver or gold in the form of realgar, particularly in the Aegean (Branigan 1974:58), and in the lower sulfide deposits as enargite and tennantite (Charles 1985:25). McKerrell and Tylecote (1972:209) regard tennantite as a common source of arsenic in antiquity.

Analyses of arsenical copper artifacts demonstrate that their arsenic content varied from less than to .25% to 4%, and even up to an occasional 10% to 12% (Wertime 1973:881). The varying percentages and types of artifacts analyzed have led some scholars to believe that arsenic was deliberately added to copper, as proposed by Caley in 1941 (60-63). There is some evidence to substantiate this view.

In 1961, a large hoard of copper objects was discovered in a cave on the west bank of the Dead Sea. Known as the Nahal Mishmar hoard, this find establishes the use of arsenical copper during the Chalcolithic Period and directly bears on the question of deliberate alloying. In a hoard of over 400 copper artifacts, including cult items and tools, 30 were analyzed. Trace element analysis showed that the arsenical copper came from the sulphide zone. Of eight tools recovered from the hoard, only one contained arsenic, while many of the cult objects contained over 5% arsenic (Key 1980:238-240, Bar Adon 1980:201). Cult objects recovered from Shiqmin in the Negev reveal a similar pattern. The everyday tools, ores and slags from this Chalcolithic site showed no traces of arsenic, while the cultic objects, similar to the maceheads, crownheads and scepters from Nahal Mishmar contained a high content of arsenic (Levy and Shalev 1989:359).

These results have led Levy and Shalev to believe that two distinct metalworking traditions existed side by side in the southern Levant during the Chalcolithic period; one for ordinary utilitarian objects, the other for cultic/prestige items. The utilitarian objects would have been made in open casts followed by annealing and hammering to work the final shape, while the cultic/prestige objects were made by the lost wax (cire perdue) method of casting.

Charles (1967:21,1979:10,1985:25)) has long advocated the idea of deliberate alloying, maintaining that arsenical minerals were deliberately selected and hand-sorted in a carefully controlled manner by recognition of their color and "garlic" odor. If arsenical copper ores were purposefully chosen as Charles suggests, why were they so desirable? Moorey (1985:16,1988:185) states that the hardness and fine, shiny, "silvery" appearance that arsenic lends to copper was superior to those of unalloyed copper. The addition of arsenic also improves the hardening capabilities of copper without causing cracking of the metal.

Arsenic improves the casting ability of copper as well. Normally, native copper is difficult to cast due to the high temperature needed to melt it, and also because it has a tendency to oxidize and form bubbles from trapped gases (Raymond 1984:26). Arsenic acts as a deoxidizing agent in copper by forming a separate metallic phase which becomes insoluble in copper and separates out from the liquid as a sublimate (Charles 1967:22). This improves the fluidity for pouring casts, particularly for decorative elements (Potaszkin and Bar Avi 1980:237).

Not all scholars agree on the deliberate alloying of arsenic to copper. Tylecote (1980:185) claims that arsenic-rich copper artifacts were the result of accidental smelting with arsenic-loaded minerals. In his view, the higher percentage of arsenic was only retained when the percentages were below 7%, otherwise if the ore contained over 7%, then much of the arsenic was lost since arsenic is volatile. Refining in a crucible would have resulted in an even greater loss as the arsenic dissipated. Thus, if an artifacts indicates a high arsenic under analysis, then the object was probably cast as soon as the metal was melted.

Charles (1967:25), on the other hand, states that only the purposeful selection of arsenic-rich minerals could guarantee any consistency for casting and workability. Based on the predominance of arsenical copper objects recovered for the Chalcolithic and Early Bronze periods, it is likely that Charles' assertion is correct.

Alloying: Tin

Arsenic was gradually replaced by tin, which became the dominant alloy to copper by the early second millennium B.C. (Muhly 1977b:75). Since there is little difference between the two in workability and hardness, the switch from arsenic to tin is puzzling. Charles (1967:26) suggests that the poisonous fumes of arsenic eventually ruled out its use. Another possibility is that the direct smelting of raw arsenical ores with copper prevented uniform casting on a consistent basis because of the varying content of arsenic in the ores. (Charles 1977:30).

When tin was first utilized or discovered remains unknown. The earliest evidence for the use of tin in the Near East and Aegean dates no earlier than the fourth millennium B.C. (Muhly 1977:76). A tin bracelet from the Early Bronze Age Level IV at Thermi on Lesbos was recovered by Lamb in the 1930s (1936:171). During the Middle Bronze Age, tin bronzes begin to show up in the archaeological record for the Near East, although there is no firm evidence for their use in Palestine until the end of the Early Bronze Age (Moorey and Schweizer 1972:192).

The archaeological evidence for pure or nearly pure tin is scarce, as well as any evidence for the mining and smelting of tin (Tylecote and Merkel 1985:12). Disintegration of tin objects from corrosion has been ruled out as the cause of its scarcity since tin is relatively stable and does not corrode easily (Charles 1977:26). A tin pilgrim flask containing 6% lead, dated to the Eighteenth Dynasty from a grave at Abydos, has been reported (Ayrton et al. 1904:50, Penhallurick 1986:9). More recently, a metal pilgrim flask from the shipwreck at Ulu Burun has been identified as tin (Bass and Pulak 1989:12). The bezel of a tin ring from Gurob from the Eighteenth Dynasty (Petrie 1891:19) was discovered, as well as a collection of clay vases covered with tinfoil from several Late Bronze Age Aegean sites (Muhly 1977a:46).

Tin in nature is found in two distinct forms, as stannite (Cu_2FeSnS_4) in copper deposits (Shepherd 1980:167) or as cassiterite (SnO_2) in fissure veins or as crystals in lode deposits in granitic rock (de Jesus 1977:33, Forbes 1964:126). While tin occurs widely in over 50 minerals, most are extremely rare or hard to recover.

Only cassiterite accounts for virtually all the tin that has been recovered (Penhallurick 1986:1). Cassiterite is exposed through weathering of the parent rock.

As a stable oxide, it remains unaltered where weathering has destroyed the host rock, leaving a concentration of alluvial or placer deposits, commonly known as stream tin (Penhallurick 1986:1), since the deposits are often found in stream beds. This remaining tin usually assumes the form of nuggets or lumps known as tin stone. Cassiterite has a specific gravity so that it sinks to the bottom of a stream bed. For this reason, it was probably collected and panned in the same manner as gold (Maddin et al. 1977:40). In fact, gold is frequently found in association with stream tin (Penhallurick 1986:xi).

Pure cassiterite contains approximately 78.6 % tin, although the percentage is usually higher in alluvial tin than in vein ores, since the agitation of a rushing stream washes the tin and removes useless debris from the dark brown nuggets (Forbes 1964:126-127). Ancient miners probably recognized cassiterite by its brown color and extreme density (Charles 1985:26).

The precise locations of the archaeological sources for tin in the ancient Near East and the Mediterranean are problematic and controversial. Present-day sources for tin are limited and not necessarily indicative of ancient sources, with the exception of obvious locations such as Cornwall in Britain. Muhly (1985:287-288) argues for a Cornwall-Aegean trade in tin, but there is currently little evidence to support this claim. Nevertheless, the implication is that the Eastern Mediterranean was dependent on faraway sources for tin (Waldbaum 1978:66).

Both Iran and Afghanistan have been cited as possible sources of tin. For Iran, however, there is no evidence to document this (Penhallurick 1986;19). A

Sumerian text mentions Zarha and BAR-gun-gun-nu as the tin mountains, but the location is unknown (Muhly 1977a:44), although the mountains of northwestern Iran have been proposed as the source (Leemans 1968:213-214). In Afghanistan, there is geological evidence for tin deposits (Muhly 1985:281). Afghanistan is also a known ancient source for lapis lazuli (Penhallurick 1986:24).

For the Late Bronze Age, Sardinia has been attributed as a source for tin. Tin is principally known from the Sardinian sites of Monte Mannu in the north and in the south at Iglesias (Figure 17), although the highly inaccessible nature of these deposits would have posed a serious challenge to the ancient miner (Penhallurick 1986:79). It appears that the Sardinian sources were not exploited in antiquity (Lo Schiavo 1988:98).

The bronzeworking industry of Anatolia may indicate Turkey as an ancient source for tin. Until recently, there was no geological evidence to support this, but an Early Bronze Age mine at Kestel in the Taurus Mountains of south central Turkey was recently discovered by Yener and her colleagues (1989:200). The site contains veins of cassiterite and placer deposits in nearby streams. Near the mine, Yener and her team located a major Bronze Age metal processing site containing 25,000 stone tools, including hammerstones, pounders, adzes, mortars and pestles (1990:xx).

By the second millennium B.C., tin composed part of the maritime trade. The discovery of disintegrated tin resembling "toothpaste" on the shipwreck at Cape Gelidonya (Bass 1967:82-83), and over 40 tin ingots and many ingot fragments found on the shipwreck at Ulu Burun (Pulak 1988:8) now provide strong evidence for this.

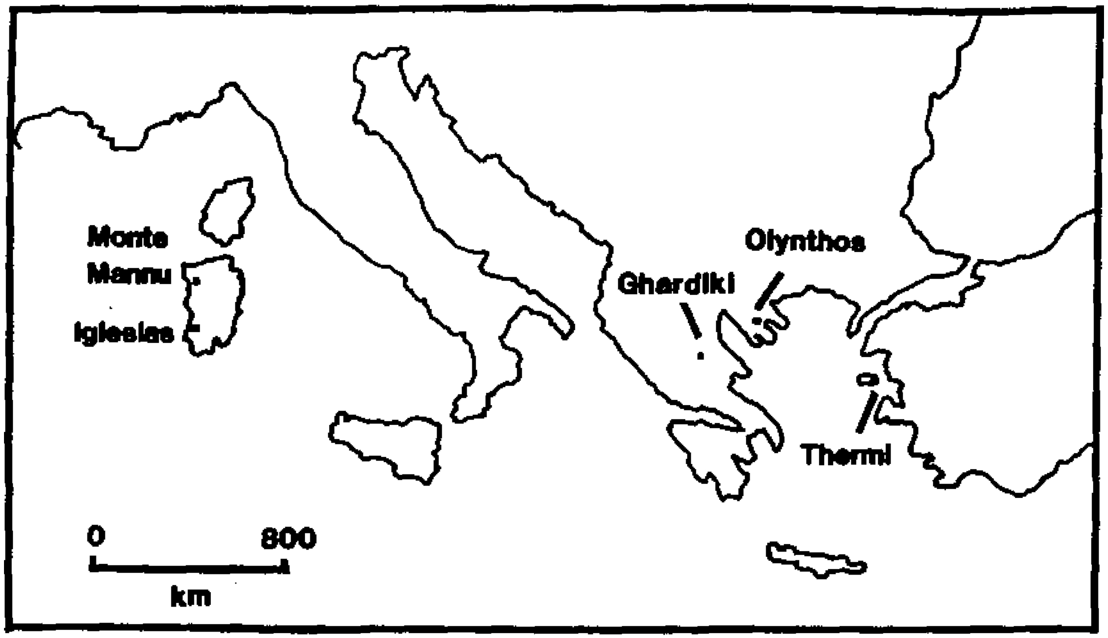


Figure 17. Map of sites located in Greece and Sardinia.

The tin trade is mentioned in an eighteenth century economic text from Mari (A 1270), during the time of Zimri Lin. The text records the incoming and outgoing consignments of tin at the palace at Mari. In this account, tin is reported to be shipped to Mari from an unspecified area to Ugarit, which served as a trading emporium between the Mediterranean and the Middle Euphrates region. The areas mentioned as receiving shipments of tin are Aleppo and Qatna in Syria, Karia in southern Anatolia, Laish (Tel Dan) and Hazor in Israel. The text mentions an overseas merchant, a Caphtorite, who is stationed in Mari. His presence there indicates trade links to the Aegean, as Caphtor either represents Crete or the general Aegean area (Malamat 1971:31, 38).

The standard ratio for alloying copper to tin in the Late Bronze Age was 9:1. How copper and tin were alloyed is not entirely clear. The addition of tin to copper may have been accomplished by adding tin as a pure ingot, or by a cementation-type process in which cassiterite was roasted then added to the molten copper in a charcoal furnace, with the metal being reduced in the melt (Charles 1977:27). The origins for this type of alloying may have begun by mixing copper and tin ores from the same gossan (Charles 1980:173).

Smelting tin from cassiterite with charcoal is a relatively simple procedure, since tin oxide melts at a lower point (232°C) than copper and can be easily reduced to metal, if strong reducing conditions are present (Charles 1985:26). These conditions would permit the direct addition of cassiterite, thus minimizing the loss of tin through a single reduction process, resulting in a single slag (Charles 1977:27).

Maréchal (1962:171-172) has shown that when copper ores with some tin content are smelted, the tin reduces in the presence of copper due to the intermetallic affinity. With the addition of 5% tin, the melting point is lowered from 1083°C to 1050°C. Adding 10% tin lowers the temperature to 1005°C, and 15% tin to 960°C (Lucas 1962:217).

It is unlikely that tin ores were directly added to smelted copper since the cumbersome ores would required being hauled long distances from mountainous regions to urban smelting centers (Madden et al.1977:41). Thus, in the Late Bronze Age, tin was probably smelted and formed into ingots at a site near the mines, then transported to secondary refining centers to be added to refined copper.

Late Bronze Age Metallurgy

To meet the demand for bronze, Late Bronze Age copper metallurgy was directed toward increased output and more large-scale operations. This included the production of pure copper ingots, which appear in the Late Bronze Age, particularly those of the "ox-hide" shape (Figure 18). Their production represents a final, refined product (Merkel 1986:251). Preliminary analysis now indicates that some of the copper ox-hide ingots recovered from the shipwreck at Ulu Burun are of pure copper (Pulak, personal communication 1991).

To refine copper requires a sophisticated furnace technology.

The best evidence for refining operations and increased copper production is found on the island of Cyprus. Evidence from Enkomi and other Late Bronze Age sites now supports the idea of secondary smelting and refining operations, devoted to melting

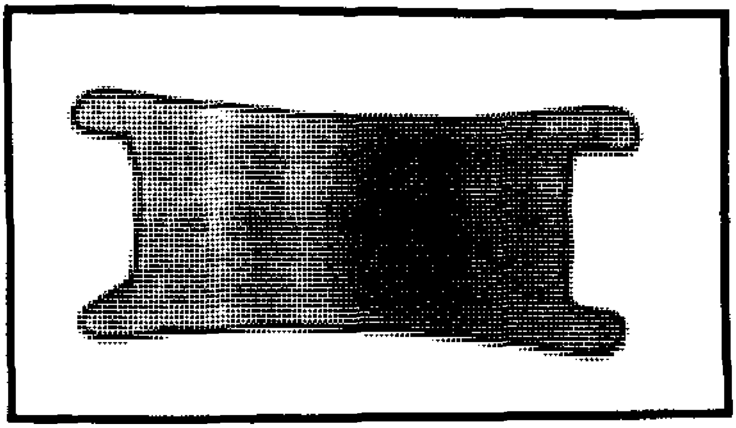


Figure 18. Example of an ox-hide ingot.

and casting (Stech 1982:105, Stech et al. 1985:401).

Catling (1964:299) states that copper metallurgy began on Cyprus in the middle of the third millennium B.C. by foreign settlers whose metallurgical tradition was well-established. According to Catling, Cypriot metallurgy was primitive as demonstrated by the lack of two-piece molds which didn't appear until the end of the thirteenth century B.C. At this time, the metallurgy tradition expands to include shaft-hole tools, sheet metal working, and lost-wax casting (Catling 1986:94). This technology improved partly due to Near Eastern and Egyptian influences (Catling 1986:99).

Actual copper mining on Cyprus is difficult to verify, although it is generally agreed that Cyprus was one of the chief copper-producing areas of the Eastern Mediterranean during the Late Bronze Age. Copper ores have been found in the Troodos Massif on the western half of the island and to a lesser extent, the area around Troulli (Bear 1963:38, Lilljequist 1969:46) (Figure 19).

Sulphide metallurgy probably reached Cyprus by the beginning of the Late Bronze Age (Wertime 1973:882), and it is likely that primary smelting was carried at or near the mining site. Mining and preliminary smelting operations on Cyprus are indicative by a widespread occurrence of slag heaps on the island (Bruce 1937:642). More than 40 heaps have been located, and the estimated total exceeds over four million tons (Constantinou 1982:19)! Recent lead isotope analysis of some Late Bronze Age bronze artifacts from Cyprus also indicates that they were made from Cypriot copper. From this, it can be suggested that tin bronze was made on

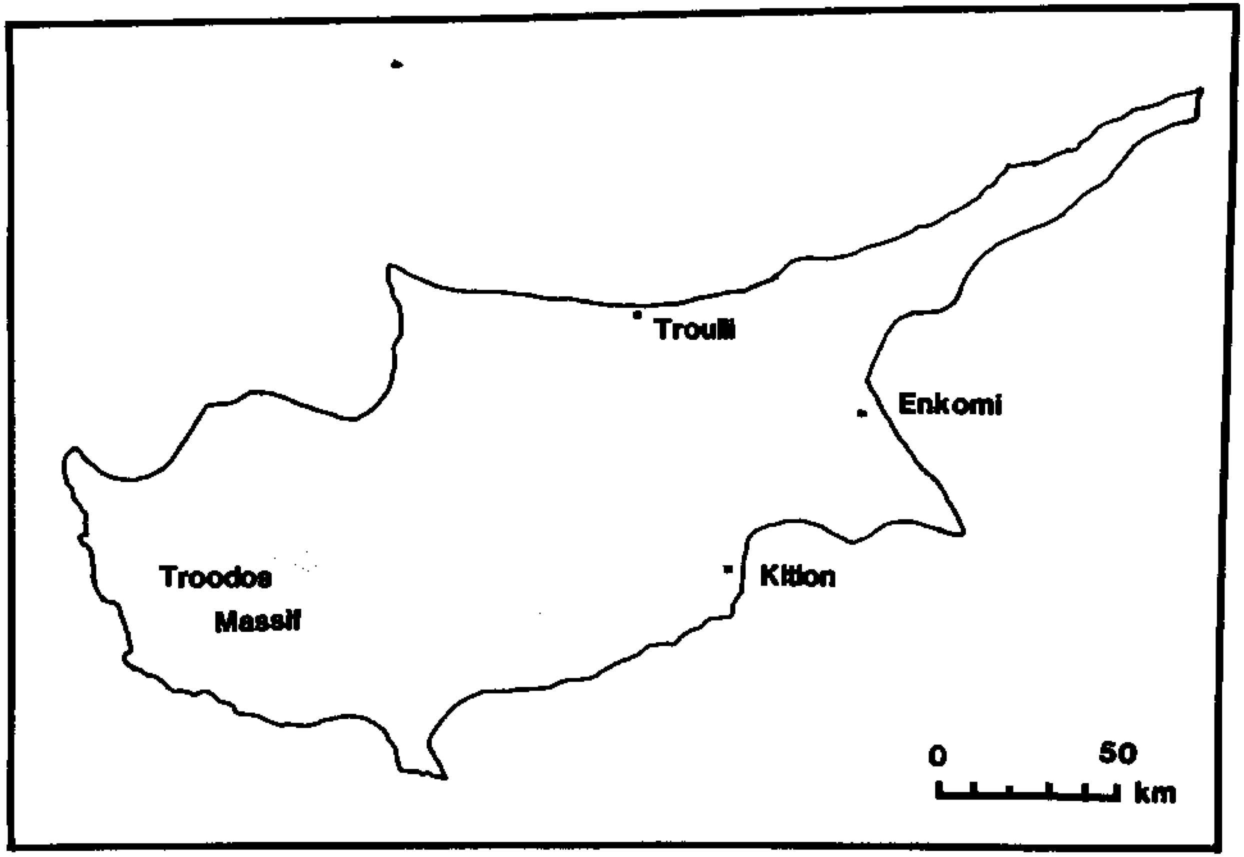


Figure 19. Map of Cyprus.

Cyprus from Cypriot copper and imported tin (Gale and Stős-Gale 1989:254).

To prepare for primary smelting, the sulphide ores needed to be roasted to remove any residual moisture and sulphide and carbonate compounds. Roasting may have been repeated several times to obtain more copper (Wheeler and Madden 1980:111, Maréchal 1985:29-30). Following roasting, the copper would then undergo primary smelting.

Steinberg and Koucky (1974:176) propose that Late Bronze Age copper smelting furnaces on Cyprus were small, bowl-shaped affairs lined with clay. The bowl-shape was designed to be placed below the charcoal in order to receive the molten copper. Primary smelting operations would be carried out for approximately an hour until small copper prills formed on the bottom of the furnace, entrapped in a mass of cinders and ash (Craddock and Meeks 1987:191). The chunks produced from the primary smelting would be glassy and blistered, so that the extra debris would have to be chipped away (Hodges 1970:71-72). The prills and enriched slags from the primary smelting sites were probably transported to large settlements where they would be smelted and refined a second time in a furnace containing bone ash. Bone ash has been discovered at Kition in pits in workshops adjacent to Temple 1 (Zwicker 1985:412). Bone ash may have been used as a fluxing agent since it lowers the melting point of slag from 1177°C to below 1000°C.

Late Bronze Age smelting furnaces on Cyprus have been found at Kition, Enkomi and other sites. At Kition, much of the evidence comes from a workshop area in Area I and a religious workshop/temple complex in Area II (Stech et al.

1985:388). Remains of crucibles, tuyeres and large chunks of slag have been excavated as well as fire-blacked cavities. At Kition, it appears that clay crucibles were used for smelting operations; unlike pre-Late Bronze Age crucibles, which were smaller, the crucibles from Kition were large with a hole in the sidewall. The inner diameters of these crucibles range to about 25 cm, the wall thicknesses to approximately 2.5 cm and the heights to 30 cm. The hole is either in the center or at the bottom (Zwicker et al. 1985:104). The hole could have been used for introducing air for refining blistered copper (Zwicker 1985:412). For alloying tin, refined cassiterite was added to the liquid copper. Remains of this process have been uncovered at Area II at Kition (Zwicker 1985:415).

The remains at Enkomi also indicate a thriving metal industry. Copper workshops have been found in Level IIB (Dikaios 1971:65). It has been proposed that Enkomi was the center of the Cypriot copper industry during the Late Bronze Age, exporting products to Egypt and the Levant, along with large amounts of Cypriot pottery (Muhly et al. 1988:294).

The secondary smelting operations may have been directed toward the production of pure copper ingots, bronze ingots and other objects. The ingots were produced in a plano-convex or bun shape, in bars and most notably in the ox-hide shape. Copper and bronze ingots have been found scattered throughout Mediterranean land sites, but the largest collections have been found on the shipwrecks at Cape Gelidonya and Ulu Burun, Turkey (Bass 1967, Pulak, 1988; 6-7). The copper ox-hide ingot trade was probably under Semitic control from the fifteenth century to the end of the thirteenth century B.C. (Bass 1967:163-167, 1973:32). The archaeological evidence indicates that ox-hide ingots were not produced before 1600 B.C., but their manufacture appears to have continued on Cyprus until the twelfth century B.C. (Bass 1973:31-33).

How copper ingots were produced is still unknown. Catling (1964:267) suggests that their design was related to ease of handling in trade, rather than for smelting considerations. Tylecote (1980:190) suggests that the plano-convex ingots were produced in a furnace where the slag was tapped at the end of the smelt to leave an ingot at the bottom of the furnace, what Rothenberg (1985:133) calls the "slag-on-top-with-plano-convex ingot-at-the-bottom model" (Figure 20). Tylecote also proposes that the ox-hide ingots were cast from a different type of furnace that included a spout or launder system (Figure 21).

Based on the Late Bronze Age furnaces found at Timna, Rothenberg (1985:133) states that Tylecote's original furnace model is oversimplified. Opie et al. (1979:17) report that tapping molten slag in a smelting furnace would have to be nearly complete and perfect in order to be successful. Any residual slag left in the furnace would lower the quality of the copper; thus a smelting furnace that could produce a 30-kg copper ox-hide ingot would demand an inordinate amount of skill (Merkel 1986:260).

Once the copper was refined, it was then poured into a mold in its molten form. How this was done is not certain. To produce a large ox-hide ingot required a substantial amount of molten copper. Numerous simultaneous pourings from

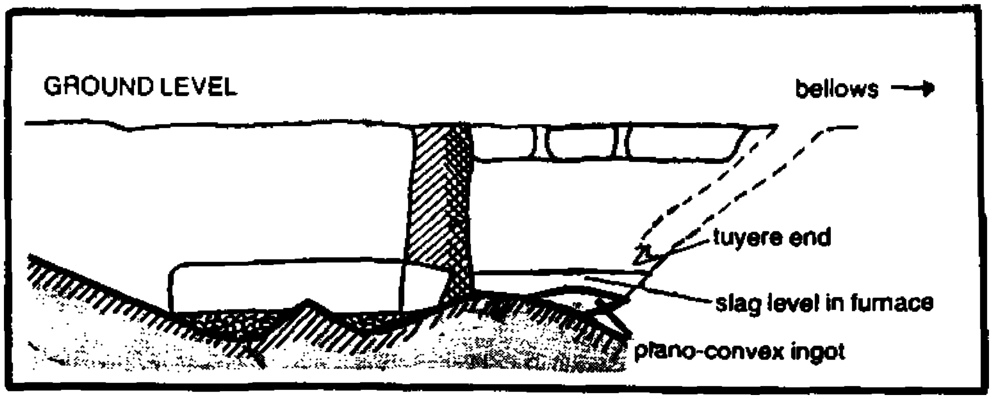


Figure 20. Copper smelting furnace for producing bun ingots (after Tylecote 1980:195).

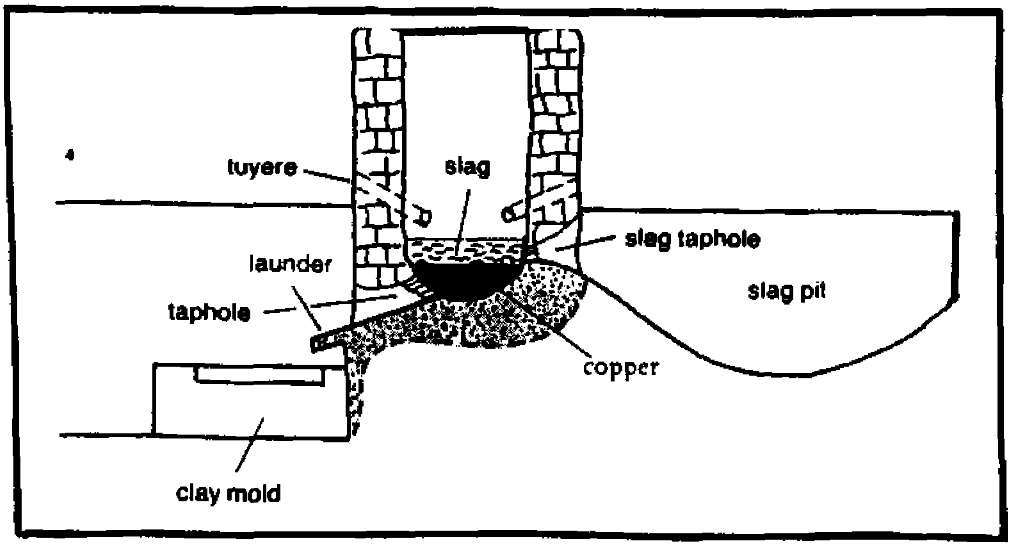


Figure 21. Copper smelting furnace for producing ox-hide ingots (after Tylecote 1980:190).

secondary smelting have been suggested, as depicted in the tomb of Rekhmire (Figure 16). This presents serious problems, however, since the cooling metal would congeal, making uniform pourings into one ox-hide mold difficult.

A more likely possibility is that refined copper was melted and poured into sand castings (Bass 1961:272), although a stone ox-hide ingot mold was recovered from a palace workshop at Ras Ibn Hani near Ugarit (Jacques et al. 1983:277).

The size and shape of the ox-hide ingots represent an advanced stage of a casting technology that dates back to the Chalcolithic Period. The earliest form is the open mold, which derives from the tradition of making mudbricks. Open molds involved carving a shape into stone. Steatite was often preferred since it is not enough to carve. The cast was made by pouring the molten metal into the carved depression (Hodges 1970:72) (Figure 22).

This type of casting is limiting, however, since the upper surface of the object has to be flat. Open molds were therefore used for flat objects which had flat surfaces, like an axe head. Surface defects could be ground off later. Another problem with open molds is the difficulty in removing the cast object after solidification. Any uneven or undercut areas of the original mold would make it almost impossible to remove the object from the mold (Steinberg (1967:10).

The concept of the open mold was carried further with the two-piece or bivalve mold, where two open molds are fastened together, with a place to introduce the molten metal (Steinberg 1967:10) (Figure 23). With this type of mold, a hollow portion could be included for creating sockets. Hollow casts also reduced the need

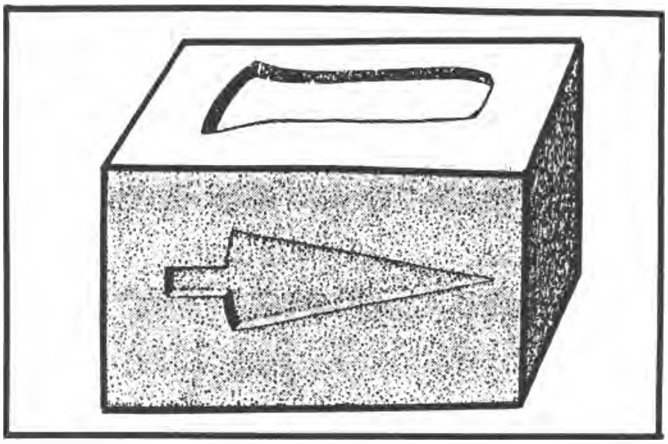


Figure 22. Open mold (after Hodges 1970:72).

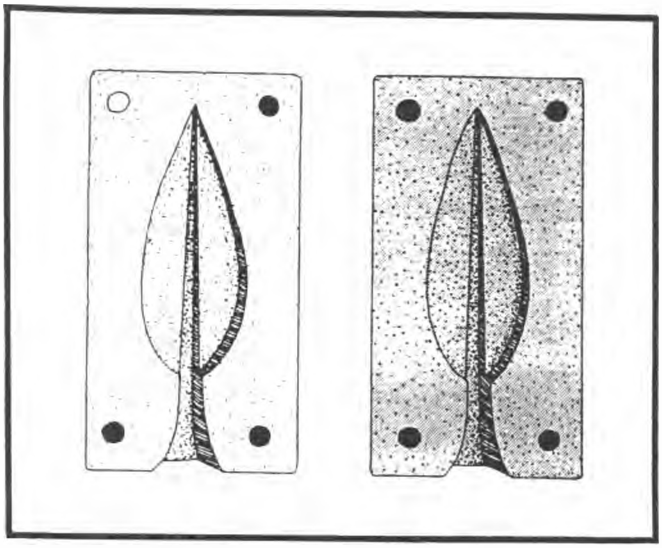


Figure 23. Bi-valve mold (after Hodges 1970:73).

for costly additional metal.

In two-piece molds, the shape was prepared from wood or clay. The pattern was then pressed halfway into the lower half of the mold, which was smoothed out and levelled and covered with soot to prevent the top half from sticking to the bottom half. Any hollow area was created by inserting a core. Sometimes dowel pins, known as chaplets, were inserted into the core's surface to prevent the displacement of the core (Coghlan 1975:53-55, Steinberg 1967:10).

The most sophisticated molding technique, the lost-wax or cire perdue method, allowed for more detailed and elaborate castings. The shape was created from a clay core which was then covered with bees-wax to accept the details. Outer coats of first fine and then coarser clay were applied and dried, then heated to fire the clay and melt and burn out the wax. Molten bronze was then poured into the cavity left by the melted wax (Steinberg 1967:11).

For hollow castings, a clay core was inserted with the mold being built over it. The molten wax was poured into the space left between the core and the outer mold (Hodges 1970:149-151) (Figure 24). Most cores were self-supporting, but chaplets were used if the cores were too weak (Coghlan 1975:62). Several chaplets have been found at Tel Nami in Area G, along with small pieces of slag, scrap metal and small pieces of lead. Lead was used to reduce the viscosity in molten bronze, thus making pouring easier for intricate molds. The addition of lead also encouraged rapid cooling which was especially important for more complicated castings (Hodges 1970:147-148).

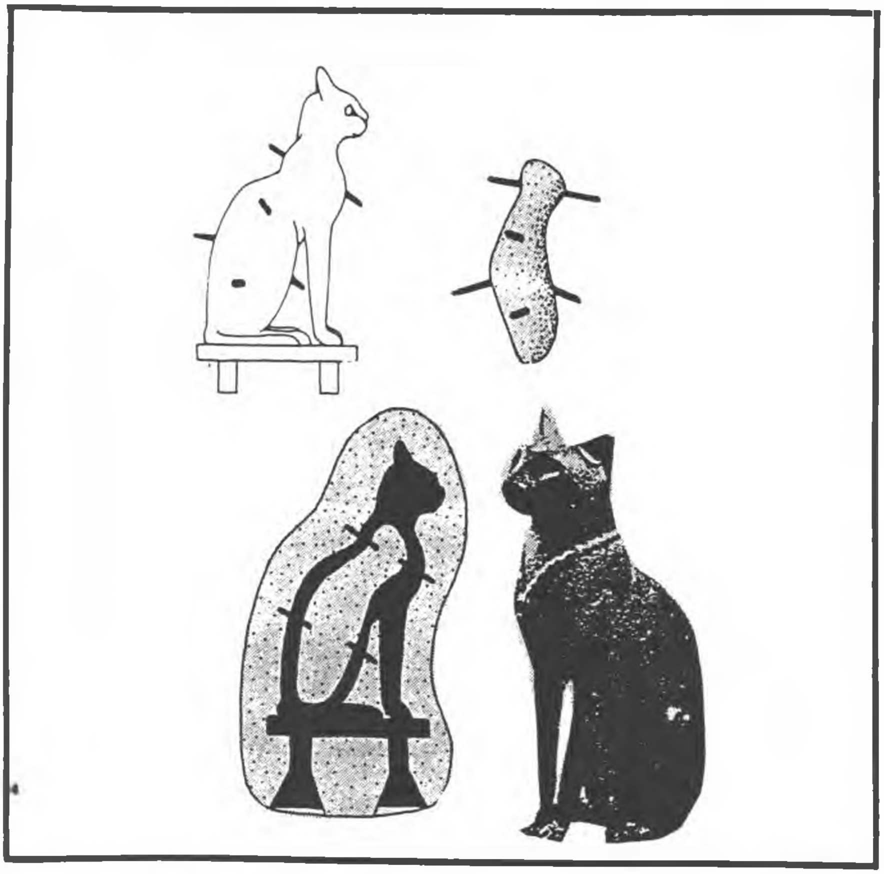


Figure 24. Lost wax mold for producing a hollow cast (after Hodges 1970:150).

Several artifacts recovered from Tel Nami were manufactured in the cire perdue method. A small bronze juglet was produced in this manner (Figure 25), as well as a small incense stand from Area O (Figure 26). Catling (1964:190-191) categorizes this type of stand into a metal tripod tradition that includes wheeled and standing tripods. According to Catling, these stands were probably made on Cyprus, although they also exhibit Near Eastern and Aegean influences in their design (1986:98). His categorization is based on their common artistic and technical traditions. Stands similar to the one from Tel Nami have been found at Ras Shamra (Schaeffer 1952: Figure 18:65), Megiddo (Guy and Engberg 1938: Plate 119) and, badly corroded, Beth Shan (Fitzgerald 1934: Plate VII, Figure 2).

The different parts of these stands were probably cast separately as component parts, either through two-piece molds or through the lost-wax method, then joined together by hard soldering. Hard soldering, also known as brazing, involved joining parts together with metal alloys requiring high melting points. The solder itself was a copper alloy such as a low-tin bronze. This produced a strong join, unlike soft solders, commonly of lead-tin, which were weak (Cronyn 1990:213, 162). Recently, a solder made of lead and tin was recovered at the return expedition to Cape Gelidonya (Bass 1989:13).

To sum up technological developments in copper metallurgy in the Near East and Eastern Mediterranean, it seems that ancient metalworkers conducted their craft with accurate knowledge of their raw materials. Early experimentation begin with the simple use of native copper ore, followed by melting and smelting technology.

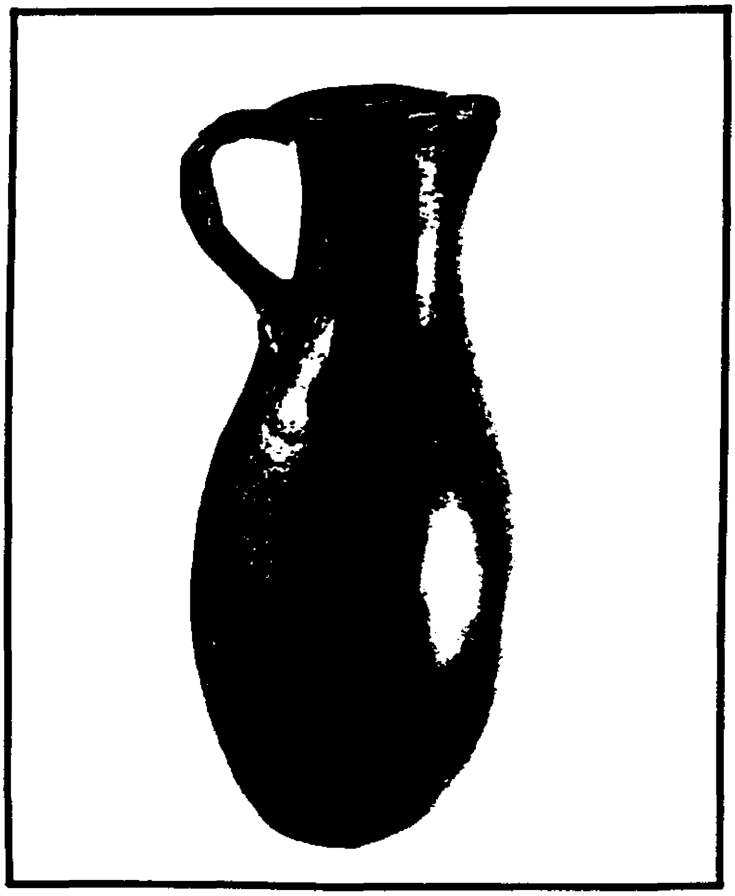


Figure 25. Bronze juglet from Area O. Length: 15.9 cm.

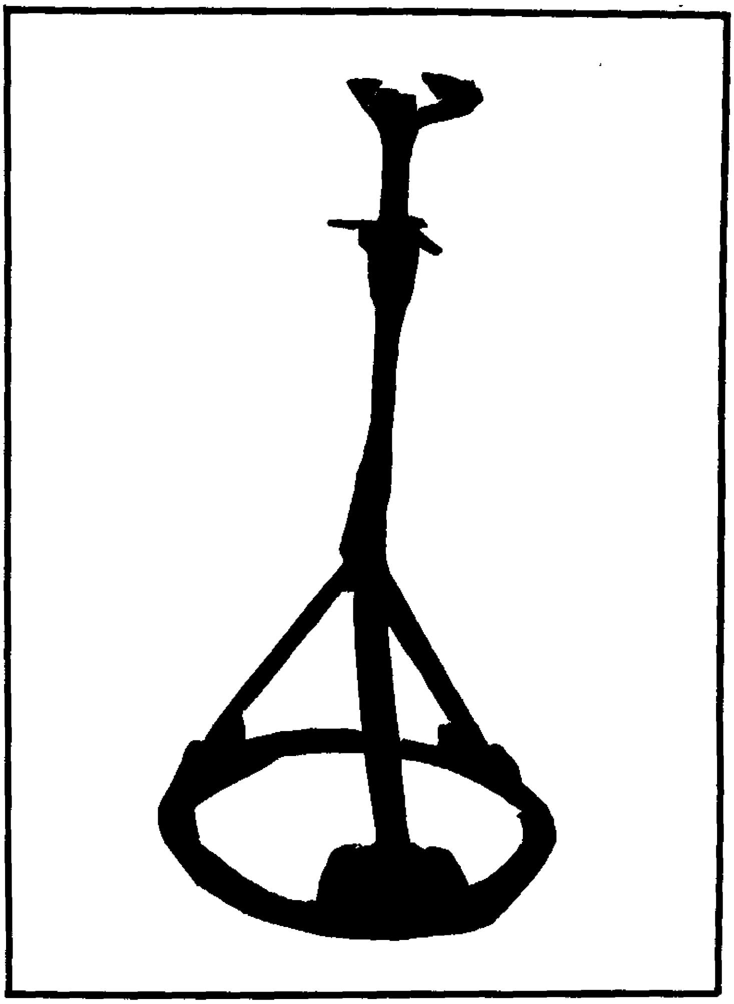


Figure 26. Tripod incense stand from Area O. Length: 18.8 cm.

Smelting technology developed from simple bowl furnaces to more complex types over a long span of time, with regional variations. By the beginning of the Early Bronze Age, alloyed metals show up in the archaeological record, as evidenced by the use of arsenical copper. By the Late Bronze Age, metalworkers have almost fully abandoned arsenical copper in preference to using tin-bronze. By this time, improvements in smelting technology also allowed for the production of large ingots which could be traded in bulk and transported by ship. The legacy of this once thriving trade is evident through the remains of copper and bronze ingots, and tools, weapons, and other objects. This legacy is more thoroughly examined in the next chapter.

CHAPTER III

THE CORROSION AND CONSERVATION OF COPPER AND ITS ALLOYS

Introduction

Removing metal artifacts from their archaeological context disturbs the chemical equilibrium that has taken hundreds or thousands of years to establish. Changes in temperature and humidity create secondary reactions, thus instigating a new phase of corrosion in a shorter amount of time than the earlier attacks which took place in situ. This presents unique problems for conservators, especially for artifacts recovered from marine sites where cuprous chlorides become concentrated in the corrosion products. The conservation of chloride-contaminated ancient bronze requires more than just a rudimentary knowledge of "kitchen" conservation (Thomson 1966:266). Rather, it requires understanding the nature of metal and the principles of metal corrosion, as well as the role environmental factors play in promoting corrosion.

The Formation and Structure of Metals

Outwardly, a piece of metal appears to be a dense, homogeneous substance. Yet, with the aid of a suitable etching reagent, a polished piece of metal under magnification exhibits a complex crystalline structure composed of crystal faces, edges, corners, boundaries and layers (Gwathmey 1948:33). Metals are made of atoms, and when grouped, form crystals known as grains. Ultimately, the physical properties of metals are partly affected by the size and shape of the grains. The crystals that form grains vary in shape and size, their external form being determined by the conditions in which they were created (Norton 1959:101).

When liquid metal cools, rapid growth occurs in particular crystallographic directions. If the liquified metal is brought to just below its melting-point, the atoms join together simultaneously in several points of the liquid mass to form several micro-crystals. The first crystal to form serves as the nucleus for other crystals to bind to (France-Lanord 1980:15). As the nuclei grow, they form branch-shaped crystals called dendrites (Figure 27). The remaining liquid metal between the branches solidifies to fill in the spaces. Each dendrite forms a polyhedral crystal with its surfaces in contact with other surrounding crystals. These clusters of crystals, which have irregular boundaries, form grains, which develop where the alignment of atoms is the same (Rogers 1964:307) (Figure 28). A relatively pure metal like copper contains only atoms of a single, metallic element that has one kind of grain structure (Norton 1959:99).

Atoms in metal are held together by forces which are electrical in nature, primarily due to the electron exchange of individual atoms. These bonds are not completely rigid, though, and should be thought of as strong springs rather than being fixed since atoms in metal are more or less in continuous motion, even at temperatures far below their melting points (Rogers 1964:94). Atoms are continually rearranging themselves to achieve the most stable configuration which is dependent upon many factors. Temperature affects atomic configuration with higher temperatures instigating thermal agitation, while cooler temperatures result in slower

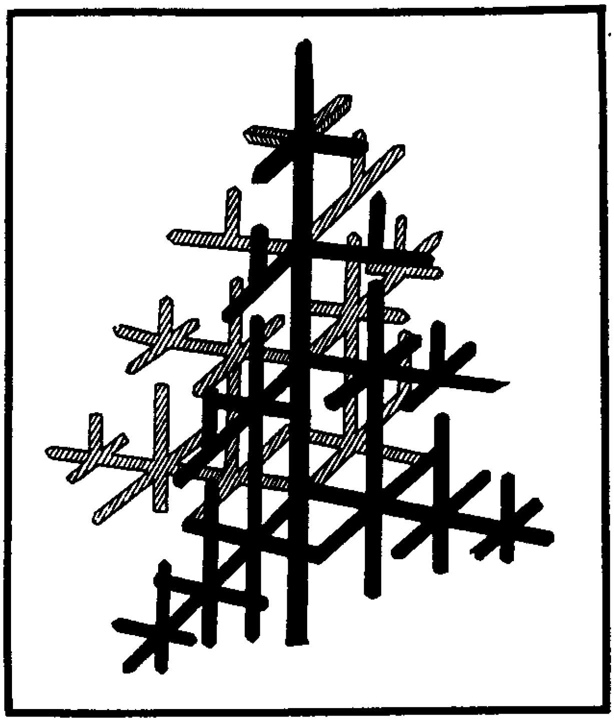


Figure 27. Ideal crystal structure in dendritic form (after Norton 1964:85).

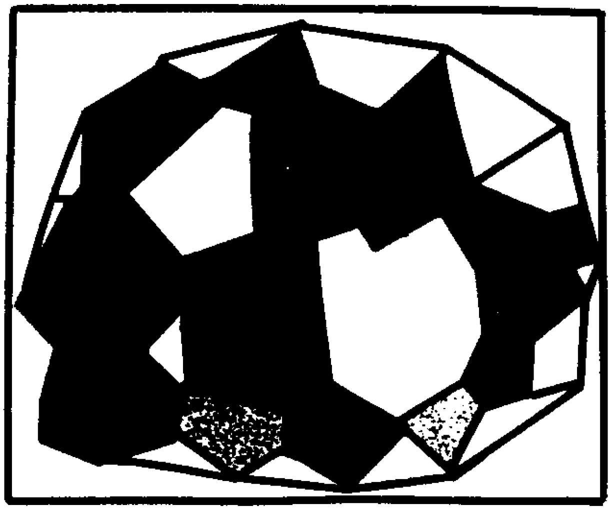


Figure 28. Grain structure of a section of brass (after Norton 1964:16).

atomic movement. This is logical if one considers that metal working is dependent on high heat to produce the malleability that is necessary to bend and shape it. Subsequent heating, known as annealing, may produce smaller equiaxial grains which contain a degree of increasing strength and loss of some brittleness.

The internal crystalline structures of metals are made up of orderly, three-dimensional patterns called lattice structures. (Figure 29). A pure metal consists of organized crystal lattice structures where atoms are packed together to achieve a state of low energy (Singley 1988:26). The most common lattice configurations are usually cuboid or hexagonal, as in copper. Lattice structure relate to metal corrosion in a specific way. Because no metal surface exists as a perfect plane, edges will exist at the boundaries of incomplete lattice structures (Figure 29). These areas may be considered "weak," where the metal is more likely to go into solution and becomes susceptible to corrosion attack (Butler and Ison 1966:7). The internal crystalline structures of alloys differ from pure metals, particularly in their homogeneity. Some metals only partially dissolve together, thus forming two or more types of grains each being a solution of one metal in the other. Other metals have complete mutual solubility in the liquid state, and hence are called solid solution metals. The different solutions in alloys are referred to as phases, and occur when metals of different-sized atoms are alloyed. Most alloys contain more than one phase, and alloys usually consist of a succession of single and two-phase regions as the composition changes throughout the alloy (Norton 1959:103). Bronze contains more than one kind of element, and therefore contains more than one structural phase. Either a solid

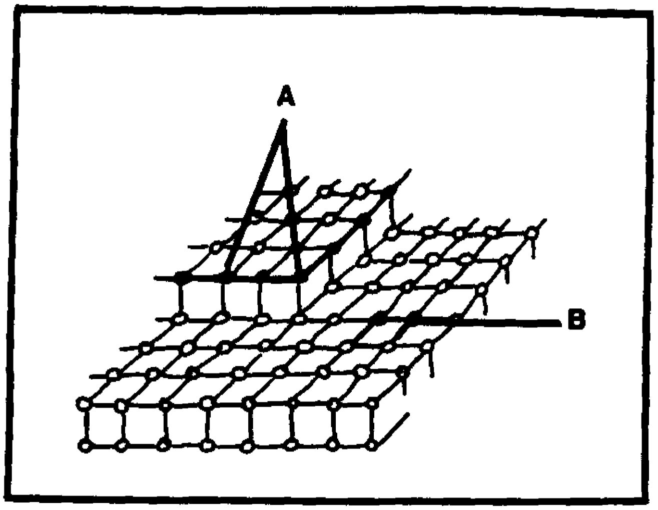


Figure 29. Example of a lattice structure. (A) represents the edges and corners of a grain boundary of an incomplete lattice plane. (B) represents a completed plane (after Butler and Ison 1966:7).

solution of two metals or a compound between two metals can constitute a phase. Phases are designated by letters of the Greek alphabet; (α) as the alpha phase, (β) as the beta phase, and (δ) as the delta phase. If two metals come from the same column of the Periodic Table with a similar chemical valence, then their solid solubility will be greater. If they come from opposite sides of the chart, then compounds rather than solid solutions will form, such as magnesium-lead (Rogers 1964:80).

Each phase has different physical properties and will contribute some of these characteristics to the resultant metal (Cronyn 1990:160). For example, phases in bronze occur in varying concentration throughout the metal so that some areas become tin-rich and others copper-rich (Dowman 1970:19). Two main factors affect phase development in bronze: the cooling rate of the molten metals and the amount of tin added to the copper (Singley 1988:26).

Usually pure metals are little affected by the rate of cooling, but, the solidification process for alloys is far less uniform so that the last portions to solidify in the cooling process may contain a smaller percentage of the predominant metal in the alloy. This results in areas of differing composition, affecting metal homogeneity. Slow cooling allows the atoms to form in a stable array and to be more evenly distributed throughout the metal.

If the alloy is suddenly quenched by plunging it into cold water, then the crystal transformation is incomplete, and the alloy remains in an unstable state (Norton 1959:107). For example, rapid cooling of bronze prevents an even diffusion of copper so that the first dendritic branches of the crystals to cool remain rich in copper, while the latter branches to solidify have a lower copper content. As a result, the metal is less homogeneous, and in some cases, surface enrichment can result where a bronze has a higher percentage of copper at the surface than in the interior (Walker 1980:277). This can be remedied by reheating or annealing the metal which restores its homogeneity by providing the thermal agitation necessary for the atoms to rearrange themselves. For bronze, the single phase can transform into α and β phases where the transformation process can become complete, and a state of equilibrium can be reached (Norton 1959:107).

Along with the cooling rate, the percentage of tin added to copper will also affect phase development and metal homogeneity in bronze. When copper is alloyed with a small proportion of tin, less than 5%, an α phase is formed in the solidification process. In the α phase, the copper-rich dendrites grow outward from the crystal nucleus, with the concentration of copper on the central portions of the dendrites, and the peripheral areas less so (Stambolov 1969:71). In α-phase bronzes, the tin is mainly dissolved in the copper matrix, but will segregate during casting so that tin becomes concentrated at the grain boundaries, the interface area where the phases meet (Walker 1980:279). Microscopic examination of a low-tin bronze often reveals copper-rich dendrites with an in-filling of tin-rich material (Hodges 1976:213).

In single-phase bronzes where the tin content is above 7%, the infilling is fairly tin-rich. This is especially true for ancient bronze artifacts. Tin-bronzes that contain up to 10% tin usually contain no inter-metallic compounds, so they are relatively soft and ductile (Hodges 1976:214). Bronzes with over 10% tin contain an inter-metallic phase, the β phase, which is arbitrarily distributed over the lattice points. This β phase is predominantly tin rich, while the alpha phase is mainly copper rich (Walker 1980:279). The occurrence of an intermetallic compound is the rule rather than the exception (Alexander and Street 1976:75).

High-tin bronzes containing over 15.8% tin, or lower tin bronzes that cool rapidly (over 6%), will form a new phase as a result of reactions in a solid solution alpha phase and the eutectic $\alpha + \beta$ phase. The eutectic phase in an alloy is the phase of the lowest melting point, characterized by a conversion of the liquid alloy into two solid constituents during the solidifying process. It can be thought of as an intermediate phase, usually a tin-rich phase in bronzes. The structure of eutectics may consist of alternate thin layers of the alloys, or as small globules of one metal embedded in a matrix of the other (Alexander and Street 1976:76). The new δ phase resulting from the α and $\alpha + \beta$ phase is not fully understood (Stambolov 1969:71).

Under the proper thermal conditions,, copper can dissolve up to 16% of tin without any change in the crystal structure, but a tin content exceeding over 25% results in too much of the β phase in the solid state. This makes the bronze brittle, which is characteristic when the intermetallic compound predominates (Alexander and Street 1976:75). Bronze objects with a tin content over 32% contain too many inter-metallic compounds of copper and tin (Stambolov 1969:72).

This raises another question. Do the various percentages of tin in copper affect the rate of corrosion? It has been proposed that when copper is alloyed with tin, the rate of corrosion increases (Plenderleith 1941:808). In bronzes containing less than 10% tin, the α-phase grains are likely to corrode first since their peripheral areas are tin-rich and are more electro-potentially negative than the copper-rich regions (Stambolov 1969:98). The interface (grain boundaries) will be the greatest points of weakness with mineralization spreading out from these areas (Dowman 1970:19). This is especially true for cast bronzes (Leidheiser 1971:73). After grain boundary corrosion sets in, corrosion will occur throughout the surface of the α-phase grains where the lattice points are occupied by atoms of tin (Stambolov 1969:98). Corrosion at the grain boundaries can actually destroy the soundness of a metal object (McKay and Worthington 1936:92), particularly objects that have been annealed (Robinson 1982:223).

Bronzes which contain a higher percentage of tin corrode differentially and have a greater tendency to corrode than low-tin bronzes. This is chiefly due to the β phase where atoms are arbitrarily distributed over the lattice points (Stambolov 1969:98), and intergranularly. Thus, disintegration eventually occurs, beginning at the outer surface, then continuing inward (Walker 1980:279). In high-tin bronzes, both the α and β phases will corrode at the tin-rich areas. In two-phase bronzes, the δ phase, which is richer in tin than the α phase, is also susceptible to corrosion (Nielson 1977:25). If zinc is present in trace amounts, the corrosion will begin at the α, copper-rich portion. If in contact with seawater, bronzes with trace amounts of zinc and some lead will undergo a two-fold corrosion which involves the simultaneous attack of both the α and β phases (Stambolov 1969:98). Hours and Michel (1973:71) examined 27 ancient Egyptian copper and bronze objects from the Louvre, and found that bronzes which contained 7% to 10% tin were fairly well-preserved, while a bronze tool with almost 17% tin was heavily corroded. They concluded that high-tin bronzes have a greater tendency to corrode.

While phase development affects the internal structure of metal, an external event, cold-working will also influence a metal's structure as well as its resistance to corrosion. Cold-working, the hammering of metal, is carried out when a metal is solid, that is, below the recrystallization temperature of the metal. In copper, cold-working affects the size and disposition of the grains. The grains in the metal become distorted and elongated in shape and the metal becomes harder and stronger than annealed metal (Newton and Wilson 1942:389, France-Lanord 1980:22). Cold-working copper during antiquity had the special advantage of producing hard and stable cutting tools.

For bronze, the more it has been cold-worked and annealed, the finer the grain structure will be. Repeated hammering results in "twins," which are pairs of identical grains whose lattice structures are mirror images of each other formed on each side of a common plane. Twins result when whole regions of atoms in a grain shift as a unit in response to the stress caused by hammering. Thus, repeated hammering causes dislocations along the crystallographic planes (Rogers 1964:216). Madden et al. (1980:225) tried to determine whether twin grains could serve as a diagnostic feature in identifying artifacts made from native copper, and decided that it wasn't possible since hammering smelted copper produces the same effect.

Cold-working is also important to consider because ancient hammered copper and bronze appear to corrode in areas where concentrated hammering has occurred (Cushing 1959:120). Cold-working and annealing processes can actually create internal structural alterations that will eventually affect the artifact's resistance to corrosion. The distortion in grains causes a change in the mechanical properties of a metal. When copper is hammered, the grains may be crushed to the extent that the copper becomes brittle (France-Lanord 1980:22). If the treatment is continued, the copper will eventually crack (Hodges 1976:73).

On the other hand, cold-working decreases the electrical conductivity of copper (Newton and Wilson 1942:389). France-Lanord (1980:22) states that cold-worked metal is more resistant to corrosion, whereas metal cast copper objects are more susceptible to corrosion attacks. The cast bronze objects found at Tel Nami refute this observation, as they were found to be in superior condition to those objects that appear to have been hammered in antiquity. Two metal sieves made of hammered bronze sheet metal, were badly corroded in comparison to three bronze incense burners and a juglet that were cast. This takes into account that these objects were found in the same area in a similar micro-environment from the same time period.

Furthermore, as cold-worked metals are commonly subject to surface tension and inner compression, this instability is concentrated at the grain boundaries, freeing metal ions, so that the metals under stress behave anodically, thus negating France-Lanord's position that low conductivity is caused by cold-working. In fact, lattice defects, caused by cold-working, can actually convert an insulating crystal into a semi-conductor. As the metal comes into contact with an aggressive agent such as seawater, the conductivity increases and a chemical attack occurs in the crystallographic planes, both in the intercrystalline areas and in the transcrystalline regions (Stambolov 1969:14).

The presence of impurities in a metal also affects its internal structure. Bronzes produced in antiquity often contain impurities reducing their corrosion resistance. Impurities present in casting affect the crystalline structure during the cooling process (Walker 1980:277). Caley (1964:5) observes that little internal corrosion takes place within alloys of high fineness since the metal below the surface is homogeneous.

One type of impurity is slag which contains some crystalline material from the siliceous components present in most ores. The slag is either found at the grain boundaries or within the grains (Cronyn 1990:161).

Iron is another impurity found in ancient bronze, either as part of the copper ore or from iron oxide that was deliberately added as flux (Walker 1980:277). The copper ores of the Troodos Massif on Cyprus are rich in iron, and ancient copper slags from Cyprus show a high iron content (Bear 1963:190-191). Craddock and Meeks (1987:202) suggest that a higher iron content in bronzes from the Near East is indicative of a more sophisticated smelting technology since lower grade ores rich in iron were successfully smelted. While the internal structure of a metal partially determines its resistance to corrosion, external factors, aside from cold-working, play a role as well in the corrosion process. These aspects will be examined in the next section.

The Corrosion Process

A non-technical definition of corrosion is "the deterioration of a metal brought about through reaction to its chemical environment resulting in the most stable compound of the metal" (Cushing 1959:110). This means that any metal is susceptible to losing electrons and reverting back to the ore which is its stable form in nature (Singley 1988:26). Iron provides an example: when exposed to rain, iron rusts. Rust is simply iron oxide, which is iron ore in its natural state. Given the proper environment, all metals will corrode, even gold, although it requires a highly oxidizing environment (Payer 1987). Corrosion is also defined as "the chemical reaction of a metal with a non-metal in the surrounding environment, with the formation of compounds which are referred to as corrosion products," (Chandler 1985:8).[4] This reaction involves a series of energy relationships that are electrochemical in nature.

Once the surface of a metal establishes contact with another substance like seawater, various places on the metal's surface develop differences in potential, creating an electromotive force that results in forming corrosion cells (Zajic 1969:22). The condition of the surface prior to and during the corrosion process will play a role in how the electrochemical process will affect the metal (Roebuck et al. 1957:89). Occlusions on the surface of a metal can encourage chemical attack, as well as areas that are shielded from atmospheric oxidation (Organ 1976:244).

Contact with an electrolyte causes the metal to react by an electrochemical exchange which is known as the solution potential of the metal (McKay and Worthington 1936:83-84). The solution potential for metals is determined by placing the metal in a solution of its own salts. Based on these observations, metals can then be arranged in order of their exact potentials. This ordering is known as the Standard Electromotive Series, based on the Nernst equation (Table 2). The Nernst scale of solution potentials enables scientists to "classify metals in order of their nobility, according to the value of the equilibrium potential of their reaction of dissolution in the form of a simple given ion considered in a standard state" (Pourbaix 1966:75). For example, magnesium, which is highly corrosive, will fizzle and dissolve when dropped into a glass of water, whereas gold or platinum at the other end of the series will remain inert in water (Payer 1987). As such, noble metals reduce more easily, but corrode less, while the more reactive metals reduce with difficulty, but corrode more (Young 1970:91).

Generally, if the electro-potential in the environment is less than the equilibrium value, then the metal is stable in its metallic state and will not corrode, but if the electro-potential is greater than the equilibrium value, then the metal will be stable only in a dissolved state, so that corrosion will occur (Payer 1987). This electrochemical relationship is likened to a simple flashlight battery. Here, a combination of two electrical conductors (electrodes) are immersed in an electrolyte which in turn creates a galvanic cell. The galvanic cell converts chemical energy into electrical energy. The electrolyte allows the current to conduct both negative and

Table 2. Standard Electromotive Series.

Element	Standard Electrode Potential **Em^0 Volts, 25 °C**
Gold	1.68
Platinum	1.20
Palladium	0.83
Silver	0.800
Copper	0.522 - 0.345
Hydrogen	0.000
Lead	-0.126
Tin	-0.136
Nickel	-0.250
Cadmium	-0.402
Iron	-0.440
Chromium	-0.71
Zinc	-0.762
Aluminum	-0.67
Magnesium	-2.34
Sodium	-2.712
Potassium	-2.922

positive carriers known as ions, which are electrically-charged atoms or groups of atoms. Ions are found in solutions of acids, alkalis and salts.

The current carried by each ion is determined by its mobility and electrical charge (Uhlig and Revie 1985:9). In order for a flow of electrons to occur, there must be a difference in potential between the negatively-charged (anode) and positively-charged (cathode) areas on the metal. This basic concept was originally introduced by Faraday (1839:230-258).

On a technical level this process is known as oxidation and reduction, where destructive corrosion usually occurs at the anode as an oxidation reaction while a simultaneous non-destructive reduction of the electrode proceeds at the cathode, usually producing hydrogen gas. The hydrogen gas may insulate the cathode from the electrolyte, so the current flow stops any polarization of the cell. Usually oxygen or some other depolarizing agent is present to react with the hydrogen, reducing this effect, so the cell continues to function (Berger 1989:3).

For example, in iron, a loss of electrons causes the metal to dissolve at the anode, while ferrous ions leave the metal and diffuse into the electrolyte solution (North and MacLeod 1987:70). Other electrons from the anode pass through the bulk of the iron to the cathode where they meet with hydrogen ions in solution which act as electronic receptors at the cathode surface. Hydrogen molecules then form at the cathode, resulting in a high concentration of hydroxyl ions which counteract the acidity of the solution. Molecules of hydrogen gas are formed, and a plating out of hydrogen occurs at the cathode, coating the iron surface with an oxide film (Cushing

1959:111) (Figure 30).

On the surface of a metal, millions of galvanic cells can form, and within a short time, providing that environmental conditions are conducive, corrosion takes place freely and on a large scale. This will continue until a state of equilibrium is reached, when the cells become polarized by a build-up of hydrogen at the metal's surface. If enough atmospheric oxygen is present, corrosion will continue (Leigh 1973:205). Corrosion may take a variety of forms that range from fairly uniform to highly localized attacks involving pitting or cracking, while other areas remain unaffected (Chandler 1985:10).

Copper and copper alloys are fairly resistent to corrosion since copper is a noble metal to hydrogen in the Electromotive Series (Uhlig and Revie 1985:327). Copper is widely used because of its resistance to corrosion and its mechanical workability and electrical conductivity.

Tin, on the other hand, is a more reactive metal, although tin compounds are more thermodynamically stable than copper compounds (Walker 1980:279). Pure tin forms a film of stannous oxide which is protective until it becomes too thick (Organ 1976:245). When alloyed together, copper and tin produces bronzes that have excellent mechanical-working abilities and good resistance to corrosion. This is evidenced by the existence of so many well-preserved bronzes from antiquity. It might be noted that on the Electromotive Scale, bronze occupies a position above copper, so that bronze can be considered more noble than unalloyed copper.

Inspite of its overall resistivity, bronze will corrode under moist or wet

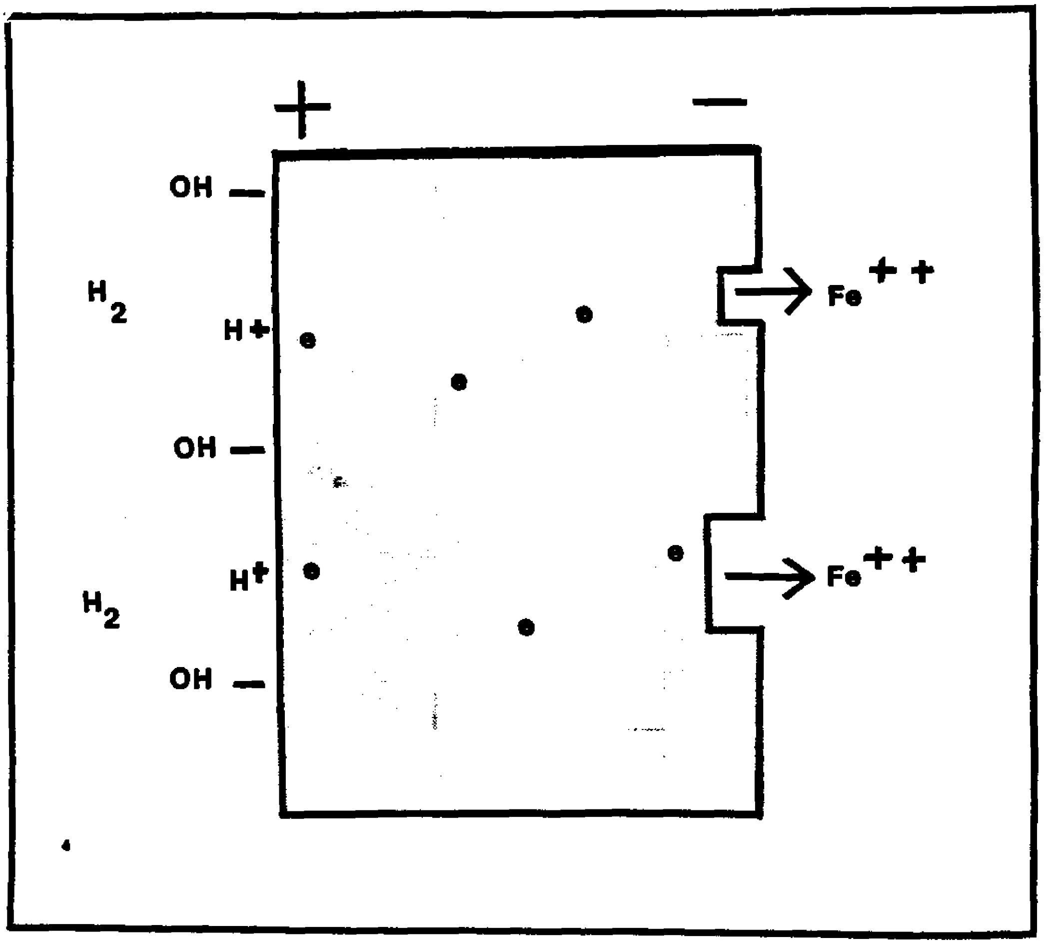


Figure 30. Oxidation and reduction reactions during electrochemical corrosion on a section of iron.

conditions since water acts as an electrolyte, promoting an electrochemical exchange. Except for arid conditions which promote good preservation, most burial environments contain some degree of moisture. For coastal and underwater sites, the continual presence of saltwater results in aqueous corrosion.

Aqueous Corrosion

Most corrosion takes place in aqueous environments. The electrical conductivity of water is governed by the amount of dissolved chemicals in the water (Cushing 1967:61), thereby making water an electrolyte that disassociates into hydrogen ions and hydroxyl ions (Goffer 1980:254). In order to determine how a solution will affect the corrosion potential of a metal, Pourbaix diagrams are often used.

Pourbaix diagrams map the regions of stability of a stable metal, based on thermodynamic calculations (Payer 1987). These diagrams only concern pure metals, however; so the behavior of alloys is unpredictable (Piontelli 1966:15). Pure water is the electrolyte standard, calculated at 25° C. Pourbaix (1966:71) identified three regions of stability on the diagram: 1) the immune area where the metal is a stable solid; 2) the corrosive area where the metal ions go into solution and; 3) the passive zone where a solid oxide or hydroxide of metal is stable.

Pourbaix diagrams also include as the coordinates the _E_ (electrode) potentials, which represents the oxidizing power of the environment, and the _pH_ of the aqueous environment. Both of these factors greatly influence the corrosion behavior of metal as a function of the environment. Plotting out the equilibrium values of _E_ and the _pH_ of corrosion reactions provides a measure of predictability for corrosion under given conditions. For example, the Pourbaix diagram illustrates the ranges of immunity, corrosion and passivation for copper in pure water at 25°C (Pourbaix 1966:389) (Figure 31).

In aqueous solutions, water purity plays a role in corrosion resistance experiments. Freshwater is less conductive than saltwater. In aerated natural waters low in anions and dissolved carbon dioxide, a protective film of cuprous oxide and cupric hydroxide forms on copper, thus retarding the rate of corrosion (Wilkins and Jenks 1948:63).

High purity water such as distilled or deionized water are slightly acidic and can attack metal (Evans 1948:4). Purity is measured in terms of electrical resistance, and in respect to having low concentrations of solids and gases (Swandby 1963:49). Solutions of distilled water may contain a high content of dissolved carbon dioxide, thus resulting in a more aggressive aqueous environment for copper and iron.

Deionized water, on the other hand, is much lower in carbon dioxide gas, so that the corrosiveness is determined by the amount of oxygen present (Butler and Ison 1966:36). For this reason, deionized water is preferred for cuprous metal conservation as the amount of oxygen can be controlled, although it is still anodic.

Seawater, unlike fresh water, is corrosive because it is high in ionic conductivity (Florian 1987:69). Seawater is a complex mixture of dissolved salts, organic compounds and gasses, and contains about 70 elements, the major components being chloride, sodium, magnesium, potassium and calcium. Several

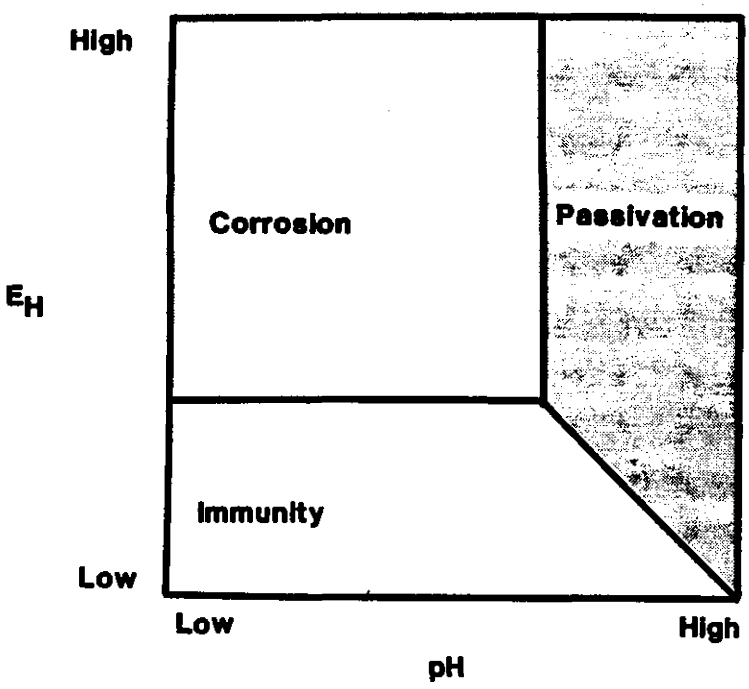


Figure 31. Simplification of Pourbaix diagram for copper in pure water at 25°C (after Cronyn 1990:169).

major factors contribute to the corrosive nature of seawater. They are: salinity, pH, dissolved gases, temperature, movement, electrical conductivity and biological organisms (fouling).

The first factor, salinity, is basically a measure of the total salt content of seawater (Weier 1973:133). The average salinity value for open ocean water is 35 parts per thousand (ppt.), but may vary between 32 and 38 ppt. at different locations and depths (Porte 1967:2, Chandler 1985:38). Salinity rates are slightly higher for enclosed seas such as the Mediterranean, the area of this study, which is 38.6 ppt. (Florian 1987:4). Salinity rates can also vary due to currents and diurnal fluctuations, and is variable at the surface, but becomes more constant with increasing depth (Weier 1973:133).

Near the mouths of rivers or in estuarine areas, seawater is often diluted. While diluted, this water is actually more corrosive because it is less saturated with respect tto carbonate solubility so that a protective carbonate layer is less likely to form on the surface of a metal (Boyd and Fink 1979:7).

The pH of seawater is alkaline, ranging from 7.5 to 8.5 (Weier 1973:136). The pH is largely determined by the presence of phosphates, borate, carbonates and silicates, and dissolved salts (Florian 1987:3), but varies slightly, depending on biological activity that consumes carbon dioxide (Boyd and Fink 1979:7). Generally, the alkaline nature of seawater itself is not corrosive, but in combination with other factors, it can contribute to corrosion activity.

Dissolved gases originate from the atmosphere, decomposition of organic material and biological activity. The two principal gasses are oxygen and carbon dioxide, and their solubility decreases with an increase in temperature and chloride levels (Florian 1987:4). The gas content is affected by evaporation, which at the sea's surface, is mixed by water movement and wind (Weier 1973:134). Dissolved oxygen usually has a maximum value at or near the surface (Porte 1967:2).

While the rate of corrosion attack usually increases with an increase in oxygen, it has been found that copper artifacts recovered from shallow wreck sites often are less corroded than those found at deeper depths. This can be explained by the presence of sulphate-producing bacteria in shallower waters which can actually form a protective layer on the metal (North and Pearson 1987:82). Also, in shallower waters, the pH remains high so that a protective carbonate-type scale is likely to form (Boyd and Fink 1979:7). Closer to the surface, objects may show more corrosion products, but are actually less corroded (North and Pearson 1987:82).

Temperature also affects saltwater corrosion. An increase in temperature will affect the chemical composition and physical properties of seawater, thereby speeding up the corrosion process, particularly in the summer months in temperate climates. Overall, temperature is inextricably linked with other factors (Porte 1967:6).

Movement between seawater and a metal can also accelerate the corrosion process (Porte 1967:6). An increase in oxygen and water movement combined can remove a protective film (erosion-corrosion), thus stimulating the production of differential aeration cells (air bubbles) (Chandler 1985:48). The air bubbles can collapse and damage the protective film (Boyd and Fink 1979:6).

The electrical conductivity of seawater is another factor contributing to its corrosiveness, and is aided by the presence of chlorides and oxygen. Seawater that is rich in oxygen is strongly oxidizing while seawater that is low in oxygen is a reducing environment (Florian 1987:7). The electrochemical reaction of cupreous metals in seawater occurs in a series of steps. The initial reaction is the production of cuprous ions which then combine with the chlorides in the sea water to form cuprous chloride:

$$\mathrm{Cu^{\circ} - e \rightarrow Cu^{+}} \qquad (1)$$

$$\mathrm{Cu + Cl^{-} \rightarrow CuCl}$$

Cuprous chlorides are unstable compounds such that, when exposed to atmospheric oxygen, will corrode a copper or bronze object through a chemical process known as "bronze disease" (Hamilton 1976:14) (Figure 32). The cuprous chloride, combined with oxygen and seawater will hydrolyze to form hydrochloric acid and basic cupric chloride (Oddy and Hughs 1970:188), as stated:

$$\underset{\text{(cuprous chloride)}}{\mathrm{4CuCl}} + \mathrm{4\ H_20 + 0_2} \rightarrow \underset{\text{(basic cupric chloride)}}{\mathrm{CuCl_2 \bullet 3Cu\ (OH)_2}} + \mathrm{2HCl} \qquad (2)$$

This hydrochloric acid then attacks the uncorroded metal to form more cuprous chloride (Hamilton 1976:14):

$$\mathrm{2\ Cu + 2HC1 \rightarrow 2CuCl + H_2} \uparrow \qquad (3)$$

$$\mathrm{4\ Cu + O2 + 4HCl \rightarrow 4CuCl + 2H2O}$$

Cuprous chlorides do not always completely oxidize in metal artifacts due to the compactness and density of successive cuprite layers, which is why cuprous chlorides are often difficult to remove (Gettens 1951:70). Cuprous chlorides cause

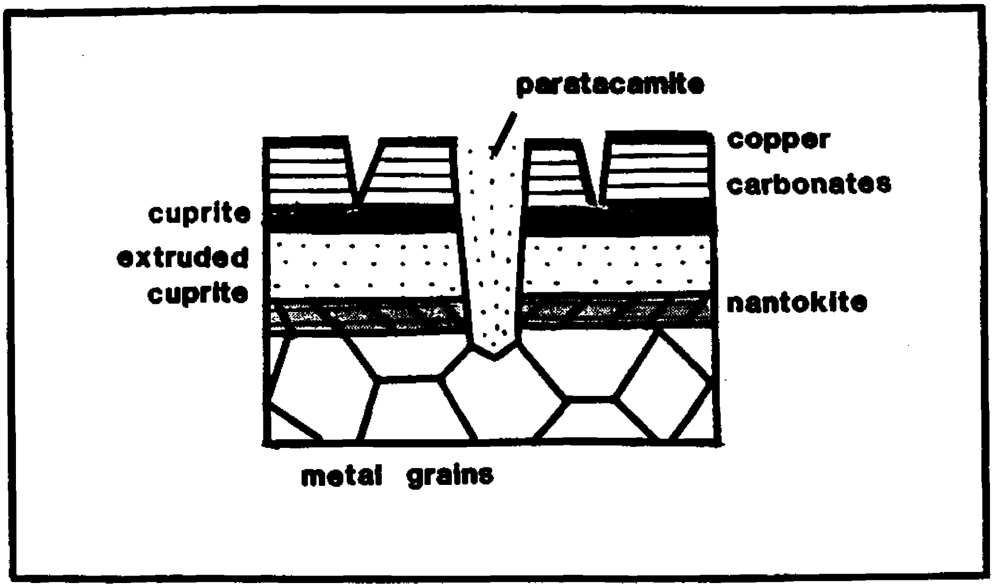


Figure 32. Example of bronze disease causing deterioration in a copper alloy (after Cronyn 1990:227).

partial or complete mineralization of an object (Hamilton 1976:14).

Marine-exposed cupreous artifacts also undergo conversion to cuprous and cupric sulphide through biological activity. The formation of sulphide corrosion products on copper objects is usually associated with anaerobic waters, where there is sand coverage or heavy sediment and sulphate-producing bacteria.

The corrosive influence of bacterial organisms was first examined by Garrett who postulated in 1891 that the corrosive action of water on lead could be attributed to the presence of ammonia, nitrates and nitrites produced by bacterial action. The nature of this type of corrosion is complex and often dependent on microbiological activity (Gerchakov and Sallman 1979:368). Bacteria will flourish in the presence of sugars, nutrients, non-organic salts and sulphates (Chandler 1985:88). Seawater, particularly estuarine water, contains sufficient bacteria to stimulate corrosion, and fouling increases with proximity to the shoreline and estuarine waters (Gerchakov and Sallman 1979:368).

The most common cause of bacterial corrosion of copper and its alloys is the sulphate-reducing bacteria, <u>Desulfovibrio</u> <u>desulfuricans</u>, which reduces inorganic sulphates to sulphides. These bacteria thrive in waterlogged coastal areas and harbors (Chandler 1985:90), and have been found on shipwreck sites where wooden hulls provide a supplementary food source for the sulphate-reducing bacteria (North and MacLeod 1987:76). For this type of corrosion to occur, the oxygen content of the water must be low. The depletion of oxygen may be due to pollution, increased microbiological activity, or burial in sand or sediment. Under these conditions, the

Eh (redox potential) falls below the hydrogen evolution potential. The main cathodic reaction in the corrosion process becomes:

$$2H^+ + 2e^- \rightarrow H_2 \qquad (4)$$

Often this reaction occurs slowly, but the action of sulphate-reducing bacteria speeds this process up, since their metabolism reduces sulphate to sulphide ions (North and MacLeod 1987:75). Sulphate-reducing bacteria can also step up the corrosion process from enzyme production of the bacteria (Chandler 1985:89) and through the formation of acids which lower the pH (North and MacLeod 1987:75).

Sulphate-producing bacteria are not always corrosive. The sulphide ions produced by sulphate-reducing bacteria form sulphide precipitates with copper ions which are toxic to sulphate-reducing bacteria, so it is unlikely that attack at the cathode will occur. As the sulphide precipitates are released from the corroding metal, a protective film on the metal's surface forms (North and MacLeod 1987:82). The sulphide layer does not adversely affect the metal, but can impart an unpleasing appearance in the form of black corrosion products (Hamilton 1976:14). If hydrogen sulfide is present, however, corrosion can take place, but to a limited degree (Robinson 1981:7). In examining copper-based artifacts recovered from sites along the Thames River in London, Duncan and Ganiaris (1987:109, 118) found that sulphide corrosion products formed by hydrogen sulphide were prone to change when exposed to high humidity.

The conditions at Tel Nami are ideal for this type of corrosion to occur, but only two objects from Area G, a piece of scrap metal and an oil lamp, exhibited black corrosion products. Future analysis may provide a more definitive explanation.

Forms of Corrosion

Once corrosion begins, it can take several forms. Of the many types of metal corrosion, six can be identified as occurring in metal artifacts. They are: 1) uniform surface corrosion; 2) galvanic corrosion; 3) localized corrosion; 4) corrosion fatigue; 5) stress corrosion cracking; and 6) de-alloying.

The first type, uniform surface corrosion, involves attack on the whole surface of the metal. It is uniform in the sense that all exposed areas are attacked at the same rate (Chandler 1985:52). Iron provides a good example, where rust covers an entire object. The result is a smooth, but etched surface with the color of freshly ground metal. Uniform corrosion was observed on many of the Tel Nami artifacts.

Galvanic corrosion takes place between two metals having different electrode potentials that are either in direct electrical contact or in close proximity in a conducive electrolyte (Hamilton 1976:8). A galvanic cell is formed with the less noble metal acting as the anode and corroding, while the more noble metal serves as the cathode and corrodes less (Robinson 1982:223).

In antiquity, copper was often alloyed with silver. Because silver is the more noble metal it is cathodic to the copper which acts as the anode. As a result, the copper plates out on the surface of the object, sometimes obliterating the silver (Dowman 1970:19). This was observed on a silver-copper alloy ring found in Area O at Tel Nami. The copper underneath the more noble silver had plated out onto the surface of the ring so that it had a splotched appearance. In archaeological materials, galvanic corrosion is also common in alloys such as tin-bronzes and iron (Plenderleith 1941:808).

Corrosion also occurs in localized areas, and damage to these areas can be severe. Localized corrosion takes many forms, and its effects are also found on archaeological metals. This was the most common form of corrosion at Tel Nami, so it is of particular interest to examine the different types and their distinctions. A good definition of localized corrosion is where one part of a metal surface corrodes at a higher rate than the rest of the surface (Scully 1975:174). A rough surface, scratches or cut edges on a metal object provides anodic areas for local corrosion to take place (Leidheiser 1971:74).

Localized corrosion transpires in a concentration cell, which is an oxygen-deprived area on a metal's surface. An example of this would be a sand deposit, and the corrosion taking place at this areas is known as a "deposit attack." The area underneath the deposit sets up a concentration cell and becomes anodic to the area exposed to free-flowing oxygen, as electrons flow through the metal to the surface outside the deposit. A cathodic reaction at the oxygen-exposed surface triggers oxygen reduction and the formation of hydroxyl ions. Pitting then results under the blocked area (Cushing 1959:118).

Pitting corrosion, another form of localized corrosion, is commonly found on archaeological metals and is often associated with the presence of concentration cells. Because extensive pitting has been observed on some of the bronzes recovered from Tel Nami, this type of corrosion is of special interest. Pitting usually takes place over a long period of time (Scully 1975:177), with the pits varying in size, depth and number. Characteristic features of pitting are a bumpy appearance, with the thickest corrosion sections covering the pits and perforated areas of the metal. Several objects recovered from Area O at Tel Nami were found in this condition.

Pitting is caused by the presence of cuprous chloride and is one of the most damaging types of corrosion to copper and bronze artifacts. Pitting occurs on all metal surfaces, but is found most often on passive alloys where the resistance of the protective film actually contains the attack in a localized area, rather than allowing it to spread. Pits can be initiated by impurities in the metal or by surface inclusions (Scully 1975:175), and is most likely to occur in an oxidizing environment where both oxygen and chlorides act as depolarizers, breaking down the protective oxide film at specific areas on the metal (Uhlig 1948:166).

Pitting corrosion was studied in 1926 by U.R. Evans, who demonstrated that pitting occurs by varying concentrations of oxygen on a metal's surface. A pit forms when the oxygen concentration is below that of the surrounding areas. Once pitting is initiated, its continuation is determined by reactions within the pit. May (1954:65-66) introduced the idea that pitting is essentially a cumulative action. Inside the pit, a small pocket of corrosive solution is trapped where a protective film is lacking. The metal inside the pocket acts as the anode, while to the areas surrounding the pocket act as cathodes.

Lucey (1967:176-179) proposes a slightly different mechanism to explain pitting corrosion whereby a pocket of cuprous chloride forms beneath a porous, electrically-conducting membrane. Copper dissolution then takes place by reaction with the anodic product beneath the membrane. Calcium carbonate is then deposited over the membrane as a result of a reaction between the chlorides with the cathodic product above the membrane (Figure 33).

Intergranular corrosion is another form of localized corrosion, and is associated with a difference in the corrosion potential of the grain boundary or the grain boundary region and the rest of the grain in the metal's internal structure. In bronze, intergranular corrosion may be either incipient or selective, depending on the micro-environment the artifact and the internal structure of the metal. In incipient corrosion, the grains are attacked, while in selective corrosion, corrosion takes place at the grain boundaries (Young 1970:89).

The grain boundary region is anodic and the attack can be severe due to the large cathodic area surrounding it (Butler and Ison 1966:56). If the attack is severe, the metal will lack a metallic ring when struck, and if the metal is bent, cracks will then form in the attacked area (Copson 1963:18). The net result is a metal that has lost its strength and ductility.

The cracks themselves create another form of localized corrosion called crevice corrosion. Inside the crack, the metal's surface is anodic to the external surface around the crack, which is cathodic (Chandler 1985:58). The cracks can be caused either by corrosion fatigue or stress corrosion cracking. Corrosion fatigue is the tendency for a metal or alloy to fracture under conditions of repeated stress at loads below its tensile strength and was first reported over 60 years ago where

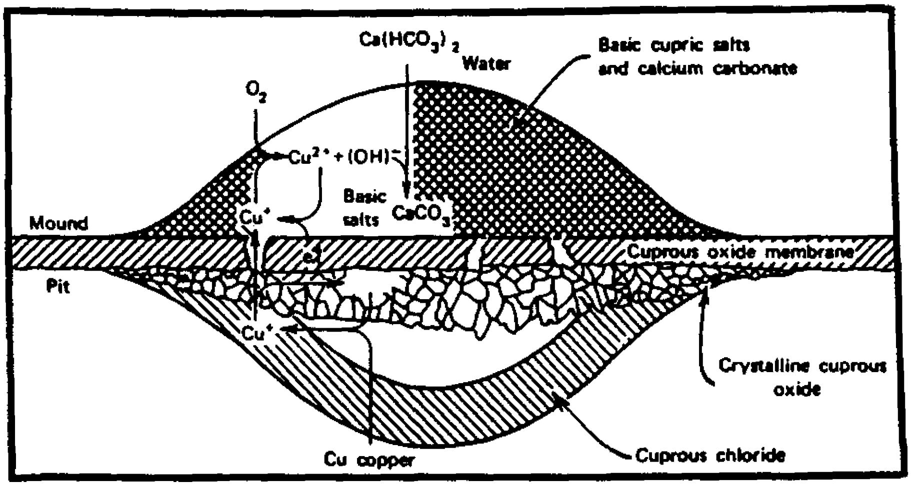


Figure 33. Diagrammatic representation of reactions and corrosion products involved in the pitting corrosion of copper, according to Lucey (from Leidheiser 1971:100: reprinted by permission of the publisher, the Electrochemical Society, Inc.).

concern arose over the deterioration of cables on the sea floor (Chandler 1985:76). Corrosion fatigue is brought about by periodic cyclic stress in a corrosive environment. For alloys, metal fatigue and corrosion together contribute to the eventual cracking of a metal. The cracks caused by corrosion fatigue occur across the grains or are transcrystalline (Cushing 1959:120) and can be found at the bottom of pits (Butler and Ison 1966:57).

Stress corrosion cracking, on the other hand, is brought about by steady pressure or static stress in a corrosive environment. These cracks are intercrystalline, and result from a combination of corrosion activity and tensile stress, in which small cracks extend outward, eventually leading to the mechanical failure of an alloy. The cracks develop at right angles to the applied stress, and copper alloys are particularly susceptible to this form of attack (Butler and Ison 1966:121). The metal at the root of the crack will eventually dissolve (Tylecote 1979:351).

Generally, stress corrosion cracking occurs under situations of localized attack rather than with uniform corrosion. Factors which play a role in this form of corrosion are environmental and the type of alloy involved (Chandler 1985:69). Stress corrosion cracking may also result from the applied stress of cold-working which weakens the internal constituency of the metal (Tylecote 1979:366).

Interestingly, the oldest known example of stress corrosion cracking is found on a Mesopotamian bronze axe, the Hasanlu Axe, a leaded 10% tin bronze dated to the third millennium B.C. The cracking was probably caused by burial in wet soil, where the wedging action of the corrosion products provided a continual source of stress to the artifact (Nielson 1977:27).

Some bronze artifacts from Area O at Tel Nami had deep cracks which were probably induced in a similar manner. The pressure and weight of sand on top of the burials in combination with the presence of seawater may also have contributed to fatigue and the eventual cracking of some of the artifacts.

De-alloying, a sixth type of corrosion found in archeological metals, is the selective leaching of one metal in an alloy from another, leaving one metal in situ. There are several types of de-alloying, such as dezinctification where zinc leaches out from brass, graphitization, the de-alloying of iron from cast iron, and destannification, the leaching of tin from bronze. When de-alloying takes place, the alloy retains its original shape, and may appear undamaged, but its tensile strength and ductility are considerably reduced (Uhlig and Revie 1985:14).

Dezinctification is the most common form of de-alloying. In dezinctification, zinc corrodes preferentially, leaving a porous residue of copper and corrosion products (Uhlig and Revie 1985:14). Brasses of more than 15% zinc are susceptible to this form of corrosion and the tendency increases as the zinc content increases (Weisser 1975:207). The surface of a single-phase alpha brass containing 70% copper to 30% zinc loses the zinc, and the dissolution of the alloy is followed by a redeposition of the copper. As a result, the object appears to be copper-rich and porous. Since no brass objects are present in the Tel Nami collection, dezinctification is not a problem.

Of even greater interest is destannification, where tin leaches out of copper in a bronze alloy, leaving behind a copper-rich matrix (Nielson 1977:26). Gettens (1951:69) reports evidence of redeposited copper in the tiny pockets of an ancient Chinese vessel. Destannification is less common than dezinctification, and has received little mention in the literature. Tylecote (1979:351) states that destannification involves either preferential corrosion and deposition of copper products on the metal surface, or internal defects in the alloy. These areas are cathodic to the alloy, particularly in areas of high tin concentration. The metal underneath these areas is then attacked, and the tin goes into solution.

Corrosion Products

The corrosion process is accompanied by its residual affects in the form of corrosion products. The study of corrosion products has become of archaeological interest in recent years since their sampling can provide information about the technology and elemental composition of ancient metal objects. Copper and bronze show a great variety in their corrosion products. They vary from thin, attractive blue-green patinas to thick, ugly crusts that can obliterate an object's original surface. The Tel Nami bronzes exhibited a variety of corrosion products. Some of them were covered in thick, mineralized crusts, while others had only thin layers.

Corrosion products serve several functions. They can act as selective membranes for the passage of ions or electrons, conducting or resisting electricity. Corrosion products also prevent or encourage contact with corrosive agents (McKay and Worthington 1936:88). Under certain circumstances, copper and bronze objects are enhanced by a mineral corrosion product. The thin, fairly uniform aesthetically pleasing blue-green "patina" associated with ancient bronze exemplifies this. This type of patina is a stable corrosion product that protects the object against further corrosion.

The amount of time required for a patina to form depends on the atmosphere. The initial oxidizing process begins immediately on exposure to atmospheric oxygen. The first stage results in tarnishing of the copper or copper alloy, which occurs within a few weeks. For a fully developed patina to form takes approximately seven years (Cieslewicz and Schweitzer 1989:126). For a copper roof to turn green may take 50 to 100 years (Walker 1980:278). Vernon and Whitby (1930:395) studied roofs of rural churches in England, and observed that patina formation goes through several stages, beginning with oxidation.

For metals to oxidize, they must be in contact with oxygen. The process is known as oxidation passivity (Organ 1976:243), where a protective film anodically. For passivation to occur, the film must be thermodynamically stable according to Pourbaix's criteria. It must adhere to the surface of the metal and be mechanically stable so that it can resist any cracking or flaking (Chandler 1985:33). A metal such as copper acquires a film of solid reaction products through adsorption of oxygen or other gasses. The diffusion of oxygen through the film then is controlled by the thickness of the corrosion product (Stambolov 1969:9) (Figure 34).

Passive films were first studied by Evans, who in 1926, examined their relation to corrosion. Since that time, two major theories have been proposed to explain how passive films are formed. The first and more popular oxide-film theory

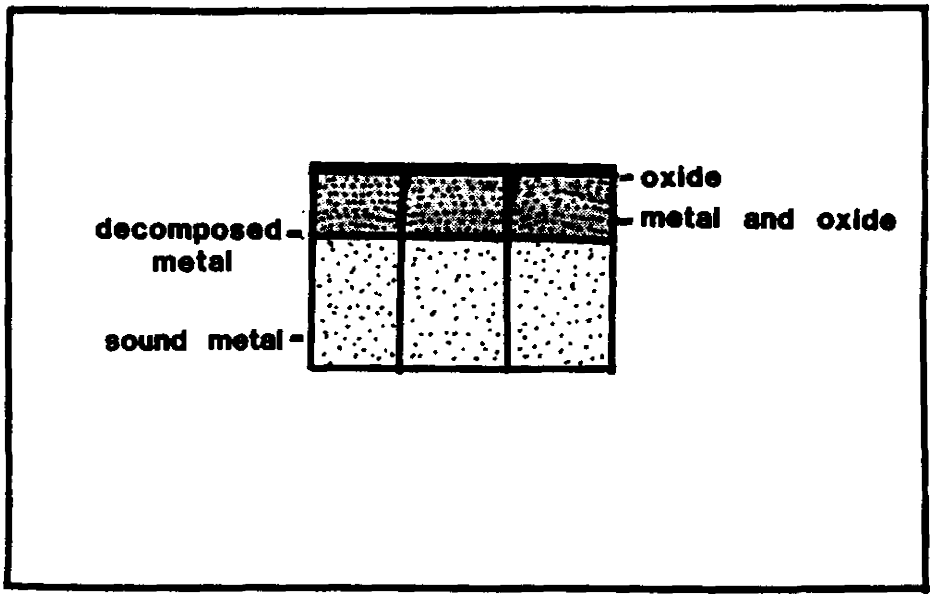


Figure 34. Stratified growth of an oxide film on a metal surface (after Stambolov 1969:17).

maintains that a passive film is a diffusion barrier layer of reaction products which separate the metal from the environment, and which slow down the rate of reaction (Uhlig and Revie 1985:69).

The other theory, the adsorption theory, states that passive are covered by a chemisorbed film such as oxygen. The oxygen displaces water molecules on the surface and slows down the rate of anodic dissolution (Uhlig and Revie 1985:70).

Passive films are of a crystalline structure, and the orientation of the film's structure in relation to the internal crystalline structure of the metal will determine whether the film will be protective or not. If the metal atoms on the film's plane match, then the film is protective (Stambolov 1969:14). If irregularities exist, then breaks in the film occur and the film is no longer protective in those areas of the breaks. Metal objects that have surface irregularities will also produce irregularities in a passive film so that its protective capabilities are reduced (McKay and Worthington 1936:94).

Passive films are also electrical semiconductors to some extent (Scully 1975:116). As mentioned previously, crystal growth in metals rarely proceeds in a perfect manner, so that defects arise in the lattice structure. The defects become have negative and positive charges. The _n_, or negative conductors possess metal in excess, while the _P_, or positive conductors, have cation vacancies and conduct electricity through the movement of electron holes where electrons are missing. These holes can move freely through the crystal in successive electron jumps (Morrison 1983:426) (Figure 35).

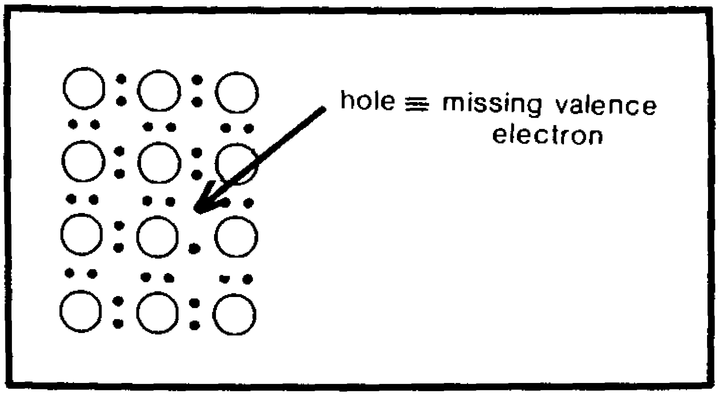


Figure 35. Example of an unoccupied valence bond (after Morrison 1983:427).

The holes at the surface can cause corrosion by becoming concentrated at the point of having two holes on the back bond of a single surface atom. Two holes on the back bond indicate that no bonding electrons are left and the bond is broken, so that the positively-charged surface becomes highly susceptible to hydrolysis (Morrison 1983:427).

Once corrosion begins, continuous corrosion products in stratified layers form. This is a complex process and not completely understood. Bands of metal corrosion have long intrigued scientists as to the nature of their formation and composition. The first scientific investigation of corrosion layers was conducted in 1826 by J. Davy, who tried to identify the chemical constituents of the corrosion products to the underlying metal. He also investigated the possible use of studying patinas to ascertain an object's authenticity (Lewin and Alexander 1967:201).

One of the first attempts to identify the minerals in corrosion products was by Austin Rogers, who in 1903 examined thousands of Chinese coins and compared them to Roman coins. Fink and Polushkin (1936) pioneered studies in establishing the relationship between corrosion and metal structure. They introduced the idea of corrosion products being banded structures. They also determined that the bands appeared in an order of the oldest being closest to the outside of the object, while the younger layers were closest to the metal surface. Fink and Polushkin also observed that different types of corrosion can exist on one object alone, specifically on cast bronzes.

One of the leading figures in studying the constituents of corrosion bands has been Rutherford Gettens. In 1951, he suggested that by studying the corrosion bands and mineral products of ancient bronzes, the mechanisms of corrosion might be better understood. In 1964, he produced a useful taxonomy of corrosion products found on copper, tin, lead, silver and iron that is still being used.

In bronze artifacts, layers of encrusted corrosion products develop as the products of the initial corrosion diffuse outward from the metal and fresh solution diffuses inward. A new supply of reactant makes its way to the fresh surface of the metal through the corrosion layers (McKay and Worthington 1936:93). As the corrosion process continues, a once ductile metal becomes weak and brittle (Organ 1963a:128), or the metal can become partially or completely mineralized.

Gettens (1951:70) initially introduced the idea that a solid metal crystal structure was invaded by an ion-bearing solution, but how the ions migrated into the solid structure was unexplainable at the time. The Liesegang phenomena may provide the current explanation for this. It involves the slow interdiffusion of metallic constituents and salts present from the environment into the solid metal. This reaction or series of reactions may produce a periodic precipitation of insoluble corrosion products such as cuprite, or atacamite, which may be present in segregated or banded layers. These periodic liquid-solid reactions result in the stratification of corrosion products (Scott 1985:49). The mineral corrosion products have a greater volume than original metal, so that eventually, a thick, mineralized crust forms (Smith 1977:213).

In some artifacts, the original surface lies somewhere in between the corrosion layers (Robinson 1982:228). This was observed on several artifacts from Tel Nami.

Gettens (1951:67) observed three zones of corrosion products on an ancient Chinese vessel. The first zone, the center, consisted of areas of uncorroded metal. The intermediate zone was partially mineralized, while the outer zone was completely mineralized. Both the intermediate and outer zones were layered within themselves.

Occasionally, thick corrosion layers form only at the crust/metal interface where the details of the original surface are preserved on the uppermost layers of the mineralized metal. Sometimes the method of manufacture is preserved in the mineralized microstructure of the metal (Robinson 1982:229). Because of this, applying conservation treatments that will not disturb this diagnostic information is important, as long as the corrosion products are not destructive to the object. In highly mineralized artifacts, the corrosion products are the only available information to determine the original elemental composition of an artifact (Fabrizi and Scott 1987:131).

The rate at which corrosion products build up is determined by the rate at which water and oxygen can penetrate. For example, a chisel recovered from the arid site of Jericho appears to have developed a crusty mineralized layer which diffused inward one millimeter in 8000 years. For an unidentified bronze object recovered from a moist Roman-British site in England, a penetration of seven millimeters occurred in less than 2000 years (Organ 1970:77).

The more commonly encountered corrosion products found in copper and bronze artifacts are categorized by their mineral species. The first category includes the oxides cuprite and tenorite, both which are usually formed at the initial stage (Young

1970:89). Cuprite, also known as red cuprous oxide, is a common oxidation product when copper reacts with air (Walker 1980:278). Many copper and bronze corroded artifacts consist of this compound, which is identified by its reddish color. Bronze converted internally to cuprite becomes brittle although the original shape of the object is retained (Gettens 1970:59).

Oxides are intermediate corrosion products in the conversion of metal to the fully oxidized salts (Gettens 1970:58). They are found between any original uncorroded metal and the outer layers (Walker 1980:278). Cuprite is usually seen as a distinct red layer underlying malachite and azurite layers, and was observed in several Tel Nami bronzes. Tenorite, black cupric oxide, is usually found as an intermediate layer between copper (or bronze) and malachite, but it does not appear to form a distinct thick layer (Gettens 1970:58).

The carbonate layers consist of malachite, azurite and chalconatronite (Lewin 1973:65; Gettens 1963:89-90). The attractive green patina of malachite is a carbonate corrosion product, and usually has a compact structure (Stambolov 1969:101). The copper carbonates of malachite and azurite form as carbon dioxide slowly dissolves as carbonic acid to form these two basic salts. The initial product of carbonic acid attack is partially water soluble, which allows copper ions to be transported over the surface of the object, even into the surrounding soil. The soluble cupric compounds then slowly change into a colloidal gel with a banded structure, which is formed in blister-like concretions resembling botryoidal, grape-like clusters. Carbonated bronzes are mostly found in humid, closed areas such as burials. Although no corrosion products have been identified for the Tel Nami bronzes, it appears that some of the objects resemble this description.

Of these hydroxycarbonates, malachite forms a smooth, dark green compact layer on the surface of an object, though it is also seen as scattered, rounded masses or nodules found on the interior of bronze vessels (Gettens 1963:89), as observed on the interior of a juglet from Area O at Tel Nami.

Azurite is similar to malachite, but is blue in color. Like malachite, azurite forms a continuous compact layer, but is often observed as fine crystal aggregates scattered among patches of malachite. It is less stable than malachite and is usually found on the inside of hollow vessels from drier archaeological environments (Gettens 1970:60).

Chalconatronite was originally found on copper and bronze objects recovered from Egypt, where in some areas of the country, an abundance of alkali carbonates are found in the soil that produce this corrosion product. It was first identified by Gettens and Frondel in 1955 (64) as a bluish-green chalky crust, and was determined to be a hydrous double carbonate of copper and sodium.

Corrosion products of chlorides are found in objects excavated from saline desert soils and from marine environments. The three most common products of chloride corrosion are atacamite, paratacamite, and nantokite. Long contact with sodium chloride results in the presence of atacamite (cupric chloride). On objects recovered from Egypt and Mesopotamia, atacamite appears as a sugary-looking coating of dark, sparkling green crystals. Atacamite is a non-protective corrosion layer, so that bronzes which become covered with this corrosion product develop fissures and become distorted (Walker 1980:278).

Paratacamite is a pale, powdery green product of atacamite. Lewin (1973:64) states that if the copper salt concentration in the environment is low, then only paratacamite will be found on the object, but if the chloride level is high, then atacamite will be present as well.

Nantokite, an unstable product, is another aggressive chloride corrosion product. It is also known as cuprous chloride. It appears as a whitish, waxy substance, and is the cause of bronze disease (Walker 1980:278). Nankotite absorbs water and oxidizes to green basic cupric chloride, then swells up in lumps (Gettens 1970:61). Copper artifacts found on shipwrecks off the coast of Western Australia have been found to contain nantokite as one of the main corrosion products, along with atacamite and paratacamite (North and MacLeod 1987:81). These corrosion products have been found both on the surface and deep down in the crevices of the remaining metal of recovered artifacts (North 1987:232). It is highly likely that these corrosion products are present on the Tel Nami bronzes.

Sulphates, sulphides and nitrates are less common corrosion products found on ancient bronze. As mentioned previously, sulphates and sulphides are associated with sulphur-bearing waters or air-borne industrial pollutants, and are often black in appearance. In bronze, the presence of tin can create stannic oxide, which is found in the corrosion bands of bronze objects. Stannic oxide is usually found in high tin bronzes and has a whitish appearance, but can appear as green or bluish green due to the presence of copper salts. Stannic oxide is formed in situ, and has been found in layers of malachite on corroded bronzes (Walker 1980:279). Alkaline conditions provoke the release of hydrogen ions in stannic oxide, which produces stannic acid. The amount of stannic acid increases with respect to the copper constituent of the bronze, although the stannic acid maintains the original shape of the object since it does not leach out of the metal (Stambolov 1969:95).

Corrosion and the Micro-Environment at Tel Nami:

The Ecological Zones

The relationship between corrosion and the in-situ condition of artifacts is better understood when the ecological zones, micro-environment and soil conditions are defined (Rose 1975:165). By estimating how each of these factors contribute to the deterioration of an object, the conservator has a sounder knowledge of the overall deterioration processes. Tel Nami can be defined as a marine coastal environment with three established ecological zones: 1) atmospheric or suppra-littoral zone; 2) splash or sub-littoral zone; 3) tidal or littoral zone.

The first zone, the atmospheric zone, is located above the high tide line, but is still influenced by ocean activity (Florian 1987:13). In this zone, sea spray settles on a metal's surface. Saltwater deposition varies with wind and waves conditions, height above sea level and the degree of exposure (Boyd and Fink 1979:2). At Tel Nami, this zone includes Areas D, D-1 and G on the tell. During antiquity, sea mist most likely settled on the surface of bronze objects. Following burial, the objects were exposed to more chlorides through accumulated salt residue on the soil surface which percolated downward into the soil matrix with seasonal rainfalls. The presence of coastal grasses, low bushes and wild lilies on the tell are indicative of the sandy and saline nature of the soil there.

The splash zone is the more aggressive zone for metal corrosion to occur. The splash zone extends from the low tide line to the edge of the submerged continental shelf. The base of the tell, in areas D and G, are subject to splash zone activity. In this zone, seawater can corrode metals by removing a protective film by wave action or by air bubbles (Boyd and Fink 1979:2). Chloride compounds are produced as seawater evaporates, which affect metal corrosion (Florian, 1987).

The tidal zone includes the high tide to low tide mark, and is usually exposed to well-aerated seawater on a continual basis. At Tel Nami, this includes the tombolo between Area O and the tell, and Area O itself.

The Soil Matrix

While the marine zones establish atmospheric conditions for Tel Nami, the micro-environment is the primary setting where metal corrosion takes place. The micro-environment, as defined by Rose (1975:165) "is the specific environment in which the artifact is located." At Tel Nami, it is the surrounding soil matrix. The soil matrix at Tel Nami includes soils originating from offshore sand accumulation, mountain-derived alluvium and pedogenic processes which take place in situ and modify these various deposits.

The soil types of the archaeological sequences at Tel Nami are part of the coastal plain general profile, which is considered to be the Mediterranean climatic region of Israel (Dan and Koyumdjisky, 1963:12). Three main soil types are found in this area: the sandy and calcareous-sandy soils, the terra rosa-rendzina group and the alluvial soils.

The first group, the sandy soils, form the predominant soil type at Tel Nami. Most of the sand comes from the Nile (Nir 1985:507). The transport and deposition of Nile sediments can be linked to two main current systems in the Mediterranean: the main surface current from the Eastern Mediterranean and the wave-induced longshore currents near the shoreline (Emery and Neev 1960:4). Sand is found at all areas of Tel Nami, but Area O consists mainly of sand and sandy soil.

The second group, the terra rosa soils, are incorporated in some of the sandy layers found in Area O. The terra rosas are derived from hard limestones of the Upper Cretaceous, are red to brownish red in color and are clayey in texture (Zohary 1982:18). The red color is attributed to iron oxides in the soil. Their originate from alluvial fans at the mouths of valleys draining into the Carmel hills (Vita-Finzi 1978:83). Mixed in with terra rosa soil of the coastal plain is rendzina, which is a grey to brownish-grey soil derived from chalky and marly rocks and is also of transported origin (Zohary 1982:18).

The third group, the alluvial soils, are hydrogenic soils whose parent material is alluvial in origin, but their subsequent development occurred at the mouths of estuaries where fluvium from the mountains merged with marine deposits due to tidal action. The swamp deposits accumulated in a belt of coastal swamps during the beginning of the Holocene until about the end of the Early Bronze Age (Neev et al.

1987:14). The upper soil profile in Area G is characterized by this soil type, as a dense, heavy clay. This type of soil is usually poorly drained and high in salt (Finkl 1982:760). This clay is found at all areas of the site, but particularly in Area G on the tell.

The deposition of the tell's layers developed over a bedrock of kurkar sandstone with the bottom-most stratum dating to the MB IIA period. This stratum is predominantly made up of sandy soil. The LB IIA and LB IIB periods comprise the remaining soil profile in Area G.

The most notable feature of the LB soil profile is the presence of the dense clay. The clay was probably transported to the tell from the swampy area in Nami East. It appears that the clay was used as a type of "cement," which was fortified by small stones, shells and pieces of pottery. A rampart on the northern side of the tell was built with this clay, as well as foundations for buildings. A hand trowel bounces back when it strikes this material, and it takes a sharp pick to penetrate it. One of the most difficult tasks is removing artifacts embedded in this matrix, particularly mineralized or brittle bronze objects.

While the dense clay material forms the bulk of the profile for the LB IIB phase, there is also a succession of layers of sandy clay, sandy pebbly clay and a final destruction layer filled with burnt soil, ash, mudbrick, and artifacts. The occupation layers are filled with bronze artifacts, animal bones, shell, jewelry, pottery and clay objects. The site may have been abandoned at the end of the LB IIB period as the destruction layer appears to be the final phase of any habitation.

Area D-1, on the upper east side of the tell, is very similar in soil profile to Area G, except for some evidence of twentieth-century military testing. Area D, on the lower east side of the tell is made up of clay, sandy soil and sand.

Since Area O falls within the range of the tidal zone, it has been subjected to centuries of tidal inundation and sand deposition. Thus, the soil profile in Area O is very salty and sandy. A sketchy history of possible flooding from related river/estuarine activity may have affected the area in antiquity as well. That seawater inundation and flooding were concerns in antiquity is borne out by the presence of a stone sump system dated to the MB IIA period.

Soil Corrosion at Tel Nami

It is apparent that the soil profile Tel Nami is varied and complex, therefore it has posed a challenge to determine how the soil types and related factors have affected the degree and type of corrosion encountered in the bronze artifacts.

The corrosion process taking place in the soil matrix at Tel Nami is similar to aqueous corrosion since the electrolyte at the site is primarily seawater, although other factors play a role in the corrosion process. These include the electrical conductivity and resistivity of soil, soil type and porosity, temperature, and acidity or alkalinity (pH).

Electrical Conductivity

Soil is roughly composed of gases, minerals, organisms, water and air. The various mineral bases provide anodes and cathodes for ionization and electrolysis to take place (Dowman 1970:15). A metal object embedded in soil then behaves like an electrical conductor. The points of contact between the metal artifact and the soil particles are affected by particle size, water content and air supply (Stambolov 1969:38). Electrical currents in soil may be generated between the metal and soil due to a difference in potential, or current may be generated between two metal objects in close proximity (Cushing 1959:115). The electrical conductivity of a soil is partly dependent on the soil's resistivity. Soil resistivity is a measure of how easily a soil will allow an electrical current to flow through it. Resistivity also measures how effectively a soil acts as an electrolyte (Escalante 1989:86).

In dry soils, resistivity is high, but in water-logged soils, such as those at Tel Nami, oxygen reduction at the cathode is negligible, making resistivity low (Stambolov 1969:40). The lower the resistivity of the soil, the better the soil will behave as an electrolyte to promote corrosion. In low resistive soils, the surface area of the anode is larger and the attack more general, but in highly-resistive soils, corrosion is usually more localized (Escalante 1989:90). Logan (1948:450) also notes a correlation between low resistivity and a high proportion of salts, conditions which are applicable to Tel Nami.

Fluctuating wet and dry conditions in both sand and clay cause fluctuations in resistivity. In dry, semi-moist and well-aerated soils, the surface area on a metal becomes cathodic while the contact between the soil particle and the metal becomes anodic (Berger 1989:9). Daily or seasonal wet/dry conditions at Tel Nami probably contributed to fluctuations in resistivity over time at the site. Finkl (1982:760) suggests that soils located near estuaries that are subject to tidal action show a great deal of variability in conductivity, particularly since the chloride content varies under these conditions. In Area O, the chloride content may increase from March to September, during the dryer months, while during the winter months, increased rainfall and possible flooding can lower the chloride content.

Soil Porosity

Soil porosity can affect the conductivity of soil as well, and is largely determined by the proportion of sand, silt and clay particles present. Porosity also influences the diffusion of water, soluble salts and gases in soil. Between clay and sand, the two predominant soil types at Tel Nami, clay has the finer particle size and minimum pore volume between particles, and tends to reduce the amount of available air and water. As water enters clay soil, it takes soluble substances into solution and ion exchange begins (Limbrey 1975:58). When wet, clay is especially a poor conductor of air. Water is adsorbed as a film on each clay particle, so that clay stores water which causes it to swell to a compact mass that makes it anaerobic and less corrosive (Stambolov 1969:31). As the soils swells, the pores close up and the rate of percolation decreases.

According to Stambolov (1969:39-40), the small particles found in clay occupy a large area of a metallic surface, thus multiplying the anodic sites. With the polarization of each anodic site, the amount of corresponding cathodic sites decreases, leading to a reduced current density. Stambolov (1969:39) reasons that this makes clay less corrosive than sand, since the large particles in sand decrease the anodic polarization.

While Stambolov maintains that clay is less corrosive than sand, localized corrosion and deep pitting in bronzes can occur since the corrosion product is in a reduced state (Cushing 1959:114), which is more damaging than uniform corrosion. Poorly aerated clay soils are also more damaging if the soil contains sulfate-reducing bacteria or a high concentration of chlorides. For example, poorly drained adobe soils with a high chloride content in California have shown to be very corrosive (Uhlig and Revie 1985:179-180).

Bronze objects found embedded in the heavy clay at Tel Nami were found in various states of preservation. Two small spearheads from Area G differed in their in situ condition. One was mostly mineralized with a small amount of metal remaining, and covered in a thick crust of corrosion products. The other, a leaf-shaped spearhead, was found in excellent shape (Figure 36).

Since porosity allows the penetration of air and water, it is assumed that soil corrosion is more aggressive in well-aerated soils such as sand, since sand has larger particles. This allows for increased aeration and the distribution of moisture. From this, Stambolov (1969:40) concludes that sand is more corrosive than clay since the larger particles decrease anodic polarization.

On the other hand, the porosity of sand also allows fresh rainwater to rinse salt away. In a study conducted by the National Bureau of Standards along the beach at Cape May, New Jersey, steel piping showed good corrosion resistance due to the permeability of the sand which allowed the salts to be washed away during rainfall (Escalante 1989:88).

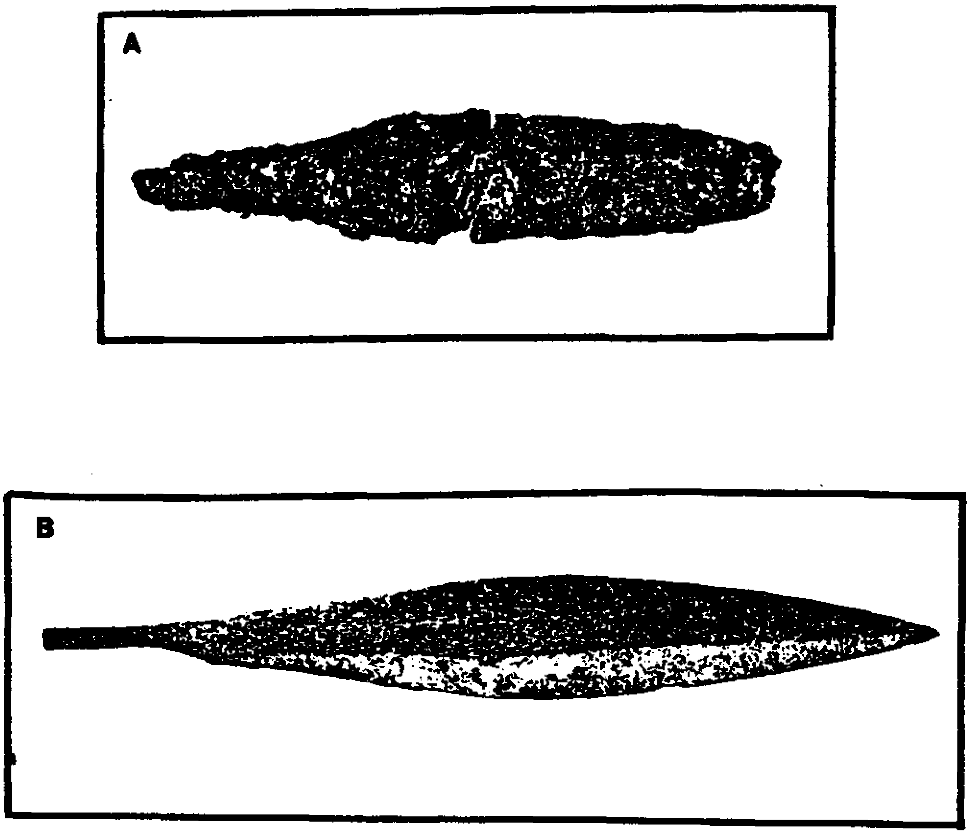


Figure 36. Comparison of two spearheads recovered from the clay matrix in Area G. (A) is heavily corroded, while (B) is well preserved. Length of A: 7 cm. Length of B: 10.8 cm.

Objects found in brown sandy soil on the tell fared well. A piece of scrap metal in the shape of a "U" from Area G, along with two scrap pieces of a hand and foot from Area D-1, and a chisel from Area D were all found in excellent condition.

The sandy soil conditions at Area O also yielded artifacts in mostly good condition. There were some exceptions. For example, a burial in Square K-5, Locus 135, excavated in 1989, was mostly composed of moist, dark sandy soil. The burial consists of gold earrings, pottery (in poor condition) and an ivory bead. The bronze artifacts, an unidentified object, possibly a mirror or knife sharpener, and a small mail armor scale plate had deteriorated to a mineralized and brittle state. A bronze ankle bracelet was also in brittle condition, with a partial metallic core. The only item found in good condition was a small knife with two rivets still in place.

Another example of poorly preserved bronze was found in Square M-6 Locus 60, the location of a grave encircled by stones. Imported pottery and a bronze oil lamp that was badly corroded and pitted were found resting against the stones. The soil profile consisted of moist sandy clay where the artifacts were found, then sandy soil, topped with sand.

The hypothesis that sand is corrosive would be supported by the condition of the bronze artifacts found in these burials. Geilmann (1956:207) notes that bronzes recovered from sandy archaeological sites are often found in a state of deterioration. He attributes this to the porosity of sand and the heavy amounts of carbonate-containing water, derived from the sand, which dissolves copper.

On the other hand, many of the artifacts in Area O were found in excellent condition. Found in sand near the baulk from the corner of Square M-5 L. 121, was a lead-filled bronze cow weight that was well-preserved except for a very tiny pit on the cow's face.

Squares M-5/M-6, Locus 80, excavated in 1988, yielded a small bronze incense stand, made from a casting, and a hammered dish that was placed on top of it. The stand was found broken in-situ in sandy soil, although it was in very good condition under the corrosion layers. The dish, however was fragile. This grave area was a succession of moist grey sandy soil on the bottom, moist sand above that, where the stand was found, topped by a layer of dry sand and bone fragments, with a top layer of dry sand covering the burial.

Another grave to yield well-preserved artifacts was Square L-6, Locus 51, the "bathtub" grave (Figure 37). This grave was constructed with large sandstone rocks in an oval shape resembling a bathtub. The grave was filled with moist sandy clay and bone on the bottom, then a layer of soft mixed sandy soil, followed by sand filled with bone, then sand. Two bronze objects, an incense bowl and a spearhead, were found in excellent condition. The dish had a substantial metallic core with a pitted and fairly smooth surface. The spearhead, which is 36 cm long, was somewhat pitted, but otherwise had a very sound metallic core.

The burial in Square L-6, Locus 69, right beneath Locus 51 contained the most extensive collection of bronze offerings, and they varied in their in-situ condition (Figure 37). These artifacts were found in the northeast corner and west side of the burial. Both areas were composed of a brown sandy soil matrix. Heavy

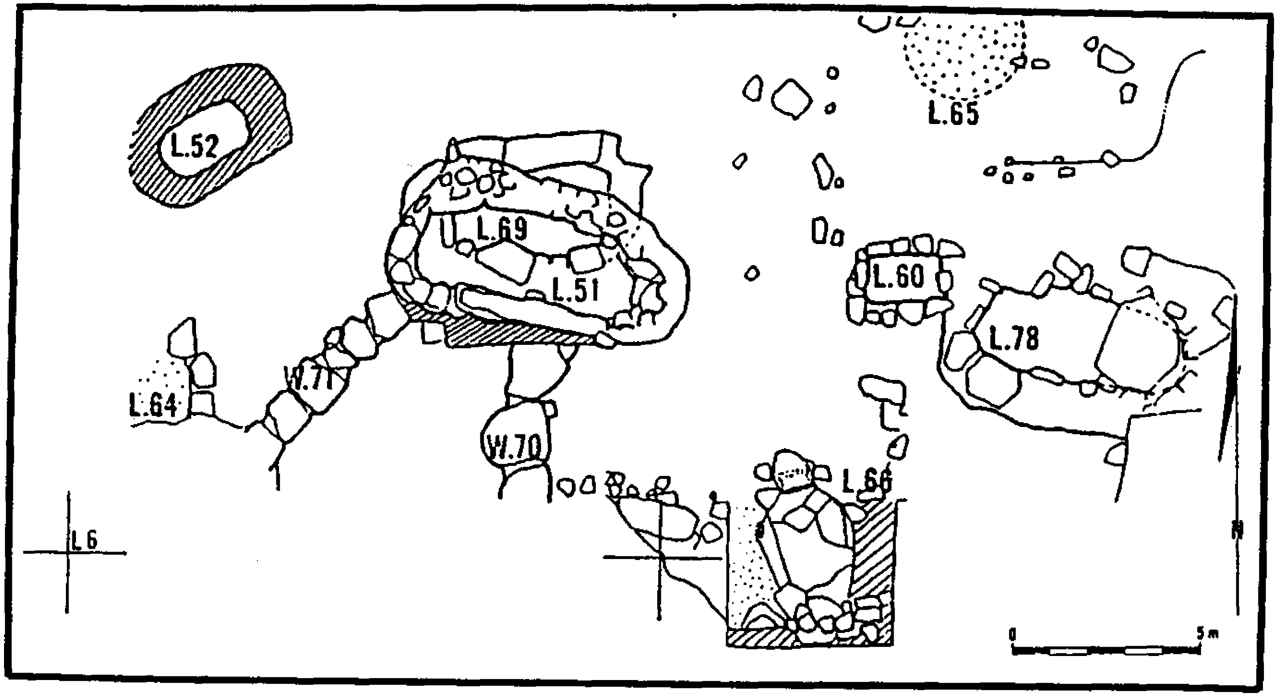


Figure 37. Section of the grave plan in Area O.

clay was used to fortify the sides of the grave, since it was found partially covering the artifacts that were lying along the edge of the grave. The clay may have washed down from the sides over time.

An incense stand with bowl (Figure 38) was found in the northeast corner of the grave. The stand was in excellent condition, covered with malachite and azurite corrosion products. The bowl, resting on the stand was bent, but intact and thin. A large oil lamp in fair condition was also found with a small bowl underneath. Toward the west side of the grave a cluster of bronzes were found stacked, including: two highly corroded, pitted bowls, one round, the other flat-bottomed; a "beer" drinking set composed of a highly corroded, thin bowl and strainer; a very well-preserved bronze base-ring bowl that had a thick metallic core; and sandwiched in between was a bronze juglet and small oil lamp with a pinched spout, both in excellent condition with no cracking or pitting.

These artifacts were covered with clay and mixed sandy grave fill. Two bronze scepters also in very good condition were found alongside the femur bones, as well as another incense stand. Dowman (1970:31) states that bronze objects found near skeletons are more mineralized on the side which has touched the body. The corrosion would be induced from chlorides that are released from the body. This was difficult to prove from these burials.

The most unusual grave was a collar-rim jar burial that was found in Area O, Squares M-5/M-6, Locus 66 (Figure 39). This large pithos was found in-situ complete and crushed. The inside contained artifacts and human bone, and was filled with a

Figure 38. In-situ condition of an incense stand from Area O.

Figure 39. Collar-rim jar burial in Area O.

brown sandy soil on the eastern side of the jar, and darker sandy clay, on the western side. A bronze spearhead (Figure 40) was found in very good condition. The spearhead is 19 cm long from tip to tip and is solid metal with striations on the top of the blade and a substantial hollow shaft. Pieces of decayed wood were found in the shaft. Analysis of the wood at the Texas A&M palynology lab was inconclusive due to the salt content and the wood's decayed state.

Ceramic burials in a similar environment have been found at Dier-el-Balah, approximately 14 kilometers southwest of Gaza (Figure 4). Located beneath sand dunes was a cemetery containing 40 anthropoid clay coffins placed in tombs cut into the kurkar bedrock, plus some scattered burials among the coffins (Dothan 1979:1). The undisturbed coffins were packed with sand covering the skeletons and burial offerings which had sunk to the bottom. Judging from the photographs and recorded observations in Dothan's published report, it appears that while several of the bronze objects were corroded and cracked, with some pieces of metal missing, the overall collection appeared to be good condition.

Temperature

The fourth factor, temperature, can promote corrosion as warm temperatures increase the chemical activity in soil (Dowman 1970:18). During the summer months at Tel Nami, the soil warms up since the weather along the coast is hot from late May to September. Escalante (1989:86), however, argues against the over-emphasis on temperature, since warmer temperatures can actually reduce oxygen solubility, reducing the rate of reaction at the cathode.

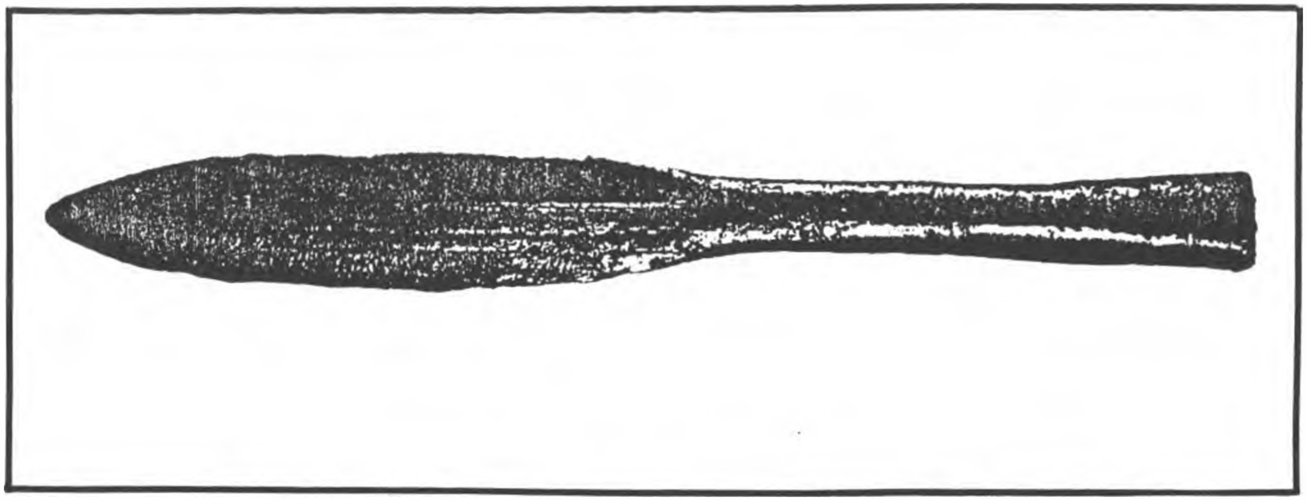


Figure 40. Well-preserved bronze spearhead from collar-rim jar burial in Area O.

Length: 19 cm.

In Area O, dune coverage may insulate the buried artifacts from any temperature increase, yet before the dunes were deposited, temperature may have affected metal corrosion more directly. On the tell, the compactness of the heavy clay and surface vegetation also insulate the artifacts from the direct effects of warmer temperatures. During excavation, the soil is cooler going down the profile.

Soil pH

The fifth factor, soil pH can also affect metal corrosion. Soils, being chemical in nature, are classified either as acidic or basic. Basic soils are rich in oxides of iron, aluminum and calcium, and range in pH from 7 or higher, while acid soils are primarily made up of silicates where the pH range is below 7. Acidic soils with a low pH can be particularly aggressive if chlorides are present. Metallic salts are produced either through the acid environment itself or in conjunction with other forces (Cushing 1959:113).

'Alkaline soils have a pH range from 7 and above and reduce bacterial activity (Scully 1975:137). Since the pH of a deposit indicates the concentration of hydrogen ions present, pH is important to consider in environments that are water-saturated. The soil pH is actually the measuring the pH of the soil solution in water-logged soils. This produces a pH reading that is higher than the true pH of the soil (Limbrey 1975:57).

Tylecote (1979:345) found that soil samples taken from sites around Great Britain showed a reasonable relationship between metal corrosion and soil pH. He concluded that acidic soils generally promote corrosion of archaeological metals, and that alkaline soils are benign, unless salts are present.

Alkaline soils, contrary to Tylecote, can be corrosive as acidic soils. Low pH soils usually affect metals that are classified as amphoteric, meaning metals that behave like non-metals in alkaline solutions. Under these conditions, they form part of a negative radicle of salt while hydrogen is given off (Dowman 1970:27). Tin is one such metal, so that in tin-bronzes, the tin will convert to soluble stannate products after a long period of time (Stambolov 1969:102). In soils where chlorides are abundant, hydrogen ions tend to displace the sodium, leaving an excess of carbonate and bicarbonate ions. This results in the pH being 9 or above. Samples taken from Area O indicated a range in pH from 8.7 to 9.2. The final destruction layer on the tell created alkaline soil conditions. A bronze oil lamp found in the temple area was located in a matrix of hard clay and sand, and the matrix was blacked from fire. The fragile oil lamp was encrusted in many layers of corrosion products, with a thin metallic core remaining (Figure 41). Could fire have affected the corrosion process?

According to Limbrey (1975:322), when organic materials burn, the mineral components left in the soil remain as ash, which is composed of alkaline earths and metals. The carbon that is produced from fire adds hydrocarbons to the soil, although the carbon itself is inert. During the fire, there is a fluctuation in oxidation and reduction of the soil potential, and the heating produces iron compounds. While the alkalinity creates neutral conditions for metal objects, the presence of the iron compounds can produce a differential in potential, with the iron in the soil acting as an anode.

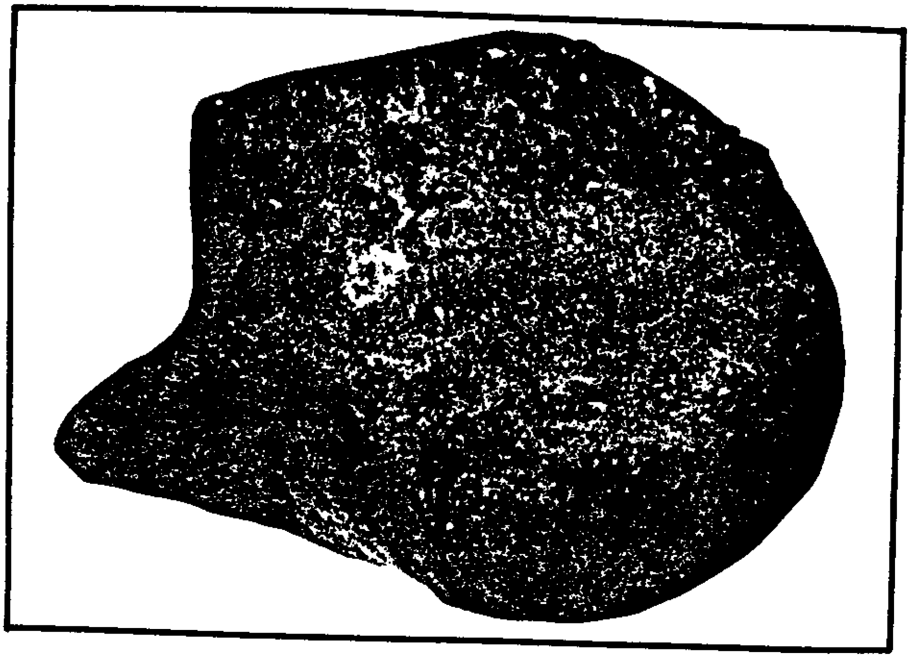


Figure 41. Heavily corroded oil lamp from Area G. Length: 15.5 cm. Width: 15 cm.

Tell Abu Hawam, a site north of Tel Nami on Haifa Bay, has conditions roughly similar to Tel Nami. Hamilton (1935:26) originally reported badly corroded bronze arrowheads found in a bed of ash and mixed debris in stratum III, the Iron IIA period. In Stratum IV, the Iron I period (Balensi 1985:68), Hamilton noted that destruction by fire had left a mixed layer of earth, ashes and crushed objects, and some bronzes found in this layer were also badly corroded. Stratum V, the LB period has five horizons separated by violent destructions, including fire (Balensi 1985:67). A pair of bronze cymbals were found stuck together, one badly corroded, the other in fair condition (Hamilton 1935:60). Thus, it appears that while fire provided the immediate and obvious destructive forces, it also created long-term alkaline conditions which, combined with a heavy clay matrix, resulted in a more corrosive environment.

Summary

In conclusion, several trends emerge from examining the micro-environment at Tel Nami. First, as evidenced by the thick corrosion layers on many of the bronzes recovered from the site, it appears that corrosion at the site was slow and continuous, eventually reaching a state of equilibrium. The initial oxide layers may have formed either before or after burial.

Secondly, it appears that objects which ranged from .05 cm and above in thickness better survived the aggressive saline environment. The composition and thickness of the metal may have provided the protection necessary to survive under these conditions. As would be expected, objects that were thin were found in a mineralized state with little or no remaining metal.

Third, very evident was the comparable difference between objects that had been cold-worked and cast. Cast items such as the incense stands, some of the bowls, the scepters, and the cow weight were found in excellent condition with very little pitting, whereas cold-worked artifacts were less fortunate. A strainer belonging to a "beer" drinking set made of hammered bronze was found to be cracked and fragile (Figure 42).

Similar sets have been found in Egypt and at Megiddo, Beth Shean and other sites in Israel (Dothan 1979:20). The strainers were cold-worked, and the holes in the strainers may have been created by piercing from the concave side with a sharp instrument while the piece of sheet metal was hot (Dothan 1979:20). Rostoker (1986:94) however, suggests that making holes in ancient sheet metal was accomplished by a series of strikes with a hammer to form a dimple, which was then worked on both sides to produce a small hole that had little or no projection on the other side. It is possible that the holes created surface irregularities which prevented the even distribution of an initial oxide film, thus exposing the artifact to localized corrosion.

As mentioned previously, cold-working distorts the internal grains and causes slippage along the grain boundaries so that the metal becomes brittle. This makes it more susceptible to corrosion attack in a saltwater environment. Stambolov's observations that crystals in the internal structure may act as semi-conductors in the presence of chlorides may very well prove valid for the cold-worked bronzes from

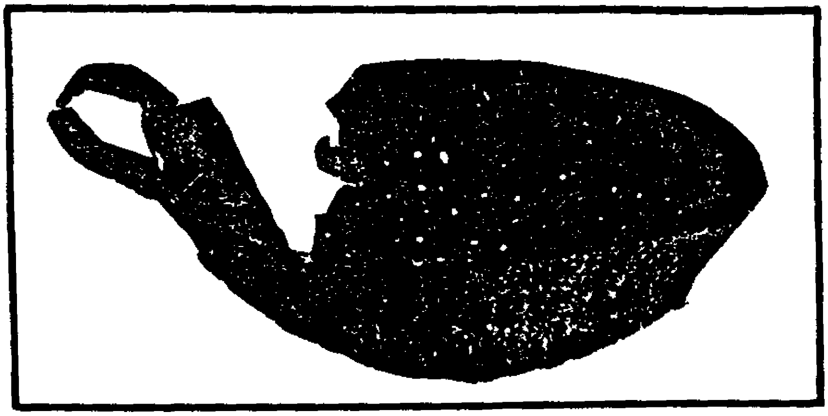


Figure 42. Strainer recovered from Area O. 10.5 cm across.

Tel Nami. These observations also refute France-Lanord's (1980:22) assertion that cold-worked bronzes are more corrosion resistant than cast bronzes. Also, the cast items at Tel Nami are of such high quality and craftsmanship that great care must have been taken in their manufacture. This would result in a finer, more homogenous internal metal structure more resistant to corrosion.

Fourth, while it appears that many types of corrosion occurred at Tel Nami, pitting and localized corrosion, plus fatigue and stress corrosion cracking were evident. Deep and extensive pitting was observed for objects recovered from Area O. This may be attributed to localized corrosion where concentration cells developed as sand particles blocked areas of a metal surface and set up oxygen-deprived, anodic areas.

Corrosion fatigue and stress corrosion cracking may have occurred as well, indicated by cracks, both large and small, as well as broken pieces of metal and bent and distorted objects. The flat-bottomed and round-bottomed bowls from Locus 69 are a prime example of this. Both were found stacked, and the flat-bottomed bowl was warped and cracked, which proved to be a challenge in its reconstruction. Both bowls were pitted and cracked from the steady, static pressure of the weight of objects on top of them. Cyclic pressure from the weight of the soil bearing down on the objects, plus their internal structure may have caused metal fatigue. The round-bottomed bowl was internally weak, such that it broke in several pieces.

Fifth, in comparing the corrosivity of sand versus clay, no definite conclusion can be drawn, yet overall, Area O produced artifacts in better condition than those recovered from the tell. A study involving buried stainless steel pipes in clay, silt and loam by Ladpo et. al. (1967:105), revealed that clay was more corrosive than loam or silt. When .3 % sodium chloride was added, the clay and silt became very corrosive while the loam remained the same. Soil resistivity increased up to 55% for clay with additional water. These observations are contrary to Stambolov's (1969:38, 40) assertion that clay is less corrosive than sand.

At Nichoria, a site located in the southwest province of Messinia in the Peloponnese on mainland Greece, bronze objects embedded in clay were found in various states of preservation. Weisser (1978:264) concludes that the bronze objects found in poor condition were embedded in a more acidic and saline environment.

Uhlig and Revie's (1985:179) position that aerated soils such as sand may be less corrosive since objects can develop a protective crust may bear out for Area O. The water table is low in Area O, and artifacts buried there are subject to moist, saline conditions, therefore the most important factor bearing on this is oxygen availability. The excellent state of preservation for several of the artifacts in Area O might be attributed to the anaerobic conditions produced by the insular nature of the dunes covering the area.

The porosity of the sand would allow some circulation of air, but it would be limited enough to slow electrolysis. This would also explain the presence of thick corrosion crusts developing over a long period of time, since less oxygen availability would reduce the rate of corrosion. Sulphate-reducing bacteria may have been active at one time in Area O, but black corrosion products only appear on a few objects recovered from the site, mostly from Area G, where the soil is highly anerobic.

Overall, the presence of seawater at Tel Nami involved a complexity of factors that contributed to in situ corrosion. The end result was chloride contamination of the bronze artifacts. Thus, the conservation program was designed with this in mind.

The Conservation Program

Methodology

As discussed, the corrosion layers of marine-exposed bronzes are chloride-contaminated when thick corrosion layers act as sponges, therefore making the corrosion products more deleterious to the artifact's stability. Because of this consideration, the Tel Nami conservation program was designed to stabilize the bronze artifacts by removing harmful cuprous chlorides safely and effectively. There were a number of treatments to consider in order to accomplish this. The choice depended on weighing the advantages and disadvantages of each method.

Harmful, chloride-contaminated corrosion products can either be "stripped" away by chemical or electrochemical means. Both methods require that the artifact possess a solid metal core. Chemical stripping treatments were first proposed by Lucas in 1932 (88-108). Formic acid, citric acid, EDTA-tetra-sodium and sulfuric acid all remove cuprous compounds when made into dilute solutions containing water. Alkaline Rochelle salts and alkaline glycerol have been used to remove cupric compounds in copper and bronze objects.

While these treatments are often effective, Merck (1978:20) reports that many of these reagents can etch metal. Organ (1976:249) recommends using chemical treatments sparingly for removing thick corrosion crusts. For some of the heavily encrusted Tel Nami bronzes, a 5% solution of formic acid in boiling deionized water was applied as a preliminary cleaning. While it is a general rule of conservation that deteriorated metals should not be chemically cleaned, some of the highly mineralized and fragile objects recovered from Tel Nami would have been greatly damaged by mechanical cleaning, the preferred method in many cases, thus formic acid was applied sparingly.

A recent treatment suggested by MacLeod (1987:25-32) is the use of alkaline dithionite, which is a strong chemical reducing agent. MacLeod states that alkaline dithionite, when compared to other treatments, is more efficient in removing chloride ions in the shortest amount of time. Using this technique on several sets of Graeco-Roman coins, MacLeod found that alkaline dithionite had reduced the corrosion products so that they could be brushed off to a loose copper powder, revealing the original surface inscription. He concluded that alkaline dithionite can consolidate heavily corroded bronzes and "reform" the original surface. Alkaline dithionite is also inexpensive and simple to use.

Ganorkar et al. (1988:97) recommend the use of AMT, chemically known as 5-amino-2-mercapto-1,3,4-thiadiazole. When this organic compound was applied to some corroded copper coins, it was found that AMT both removed corrosion products and formed a protective polymeric complex on the coins' surface.

Another agent used for cleaning is sodium hexametaphosphate, a sequestering agent that dissolves cupric salts more readily than cuprous salts (Organ 1963b:109). Plenderleith and Werner (1988:255) recommend it for removing calcareous deposits and malachite corrosion products by soaking the bronze in a 5% solution. Plenderleith and Werner also state that sodium hexametaphosphate may be safely used for highly mineralized bronzes. Merck (1978:20) however, reports that it attacks metal. For this reason, sodium hexametaphosphate was not considered for the Tel Nami project.

Stripping by electrochemical means is accomplished through electrolytic reduction, which unlike chemical cleaning, does not etch metal. Hamilton (1976) has discussed electrolytic reduction extensively. Jedrzejewska (1963:135) has criticized this method, claiming that it destroys diagnostic information, plus plating out of the metal can occur. All chemical treatments, however, result in some copper plating of the object. It has been shown that electrolytic reduction is one of the best methods for removing harmful cuprous chlorides. Since electrolysis removes cuprous chlorides from salt-water contaminated metal objects (Hamilton 1976:31, 61), it was included as part of the conservation program. Only those bronzes with a sound metal core were considered for treatment.

If an object had decorative elements or a patina, it was treated with sodium sesquicarbonate rather than with electrolysis. In cases where a difficult calcareous deposit was present, electrolytic reduction was more useful in removing it. Also, three objects that had been chemically stripped previous to the author's involvement were re-evaluated. Electrolysis removed a thick layer of PVA that had been previously applied to all three of these objects. Electrolysis also removed the discoloration caused by the previous chemical treatments.

Two small power supply units were purchased and modified for DC current at the Texas A&M University physics laboratory. An artifact was suspended from a brass rod with stainless steel, spring-loaded alligator clips, into a thick-walled plastic vat that contained an electrically conductive solution. The electrolyte used was a 5% solution of sodium carbonate (Na_2Co_3) in tap water. Sodium carbonate was chosen since was safer to handle than sodium hydroxide.

The set-up for electrolysis is similar to a simple electrolytic cell. The artifact serves as the cathode and a mild steel mesh screen placed in the vat acts as the anode. The mild steel mesh is connected to the positive terminal of the DC power supply by means of an insulated double-stranded copper wire, while another section of that wire connects the negative terminal of the power supply to the artifact to establish electrical contact (Figure 43). The power supply unit provides the energy to create oxidizing and reduction conditions by controlling the flow of electrons (Hamilton 1976:30).

Once the power supply is activated, the positively-charged metallic copper ions in the corrosion compounds begin to reduce back to a metallic phase and the metal is deposited on the object (Kruger 1977:64). The reduction of copper corrosion film is a cathodic reaction whereby electrons must be supplied to initiate the process. The reduction reaction for a copper oxide layer is expressed as:

$$Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^- \qquad (5)$$

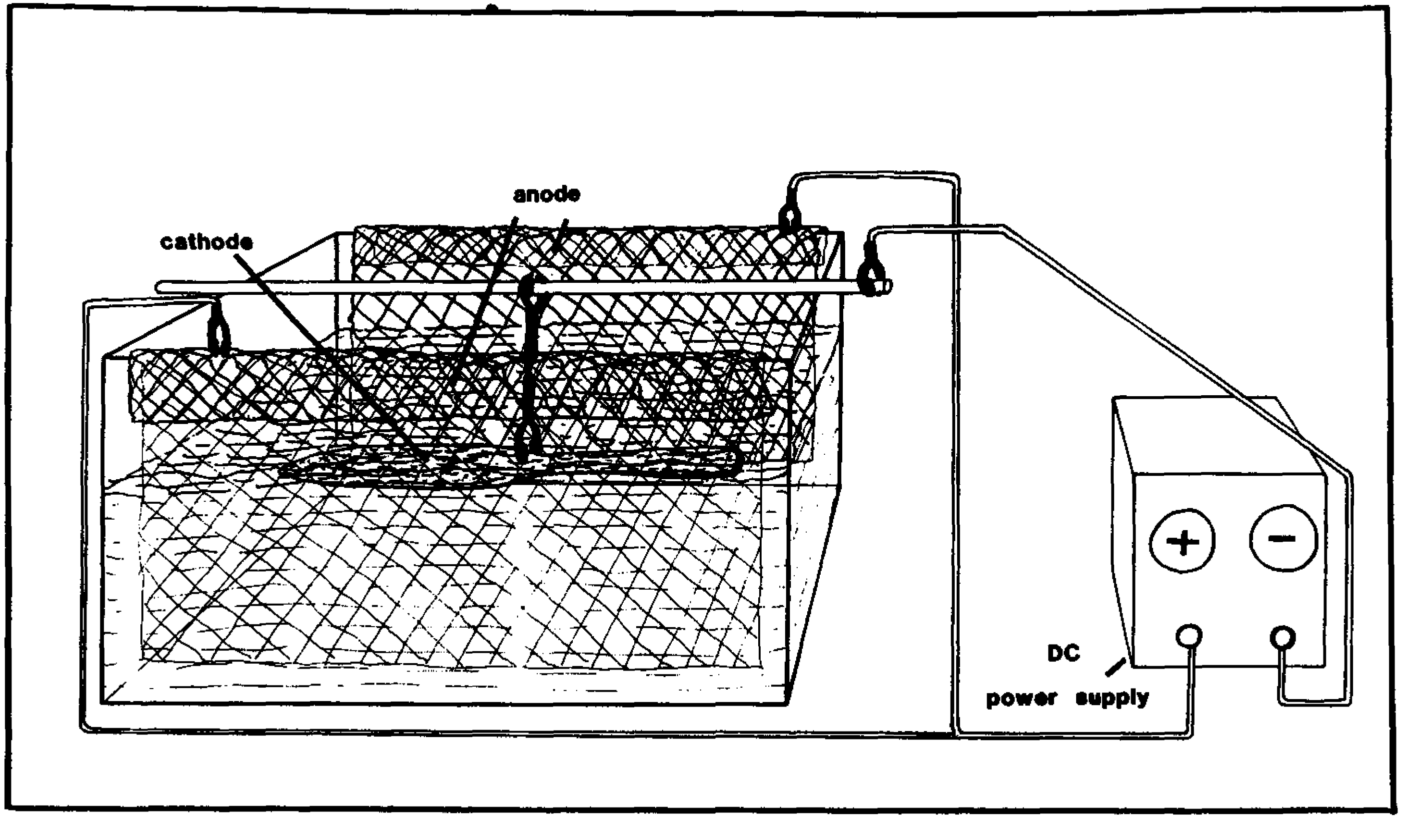


Figure 43. Diagram of electrolytic reduction set-up.

The power supply provides the necessary reduction represented by:

$$Cu \rightarrow Cu^{+} + e^{-} \quad (6)$$

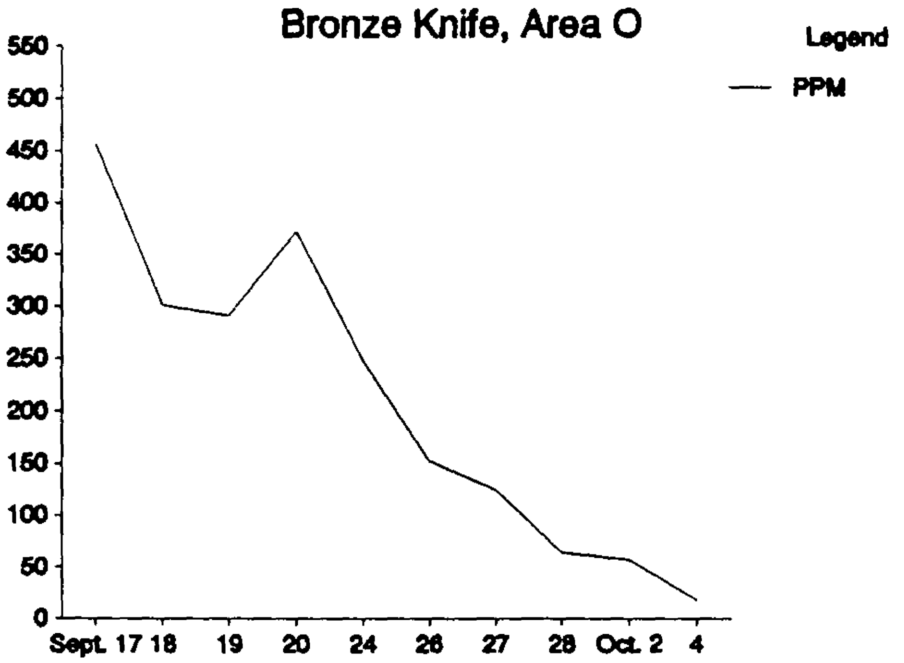
The conversion of copper compounds to denser copper metal also increases the diffusion rate of the negatively-charged chloride ions which are drawn from the object and migrate out toward the positively-charged anode by electrolytic attraction (Hamilton 1976:30, North 1987:238).

The above process was controlled by setting the current density at .02 amps per square centimeter. The current density for each object was carefully checked on a daily, and sometimes hourly basis to prevent any possible damage to the artifact. Chloride levels were also monitored daily by the mercuric nitrate test and recorded (Figure 44).

When compared to their original condition, two artifacts appeared to benefit from electrolysis. These included a bronze spearhead from Area D (Figure 45), and a dagger from Area O with its tip bent back (Figure 46).

If corrosion products or the patina are to be retained, stabilization becomes more difficult. This can be accomplished by applying silver oxide paste to localized attacks of bronze disease on the object's surface. The paste merely seals off the chlorides from the atmosphere (Hamilton 1976:60). Silver oxide is expensive, and it can darken with time (Weisser 1987:106). This treatment was not applied to the Tel Nami bronzes.

A more successful treatment involves adding alkaline agents to water such as sodium carbonate or sodium sesquicarbonate. Because cuprous chlorides are



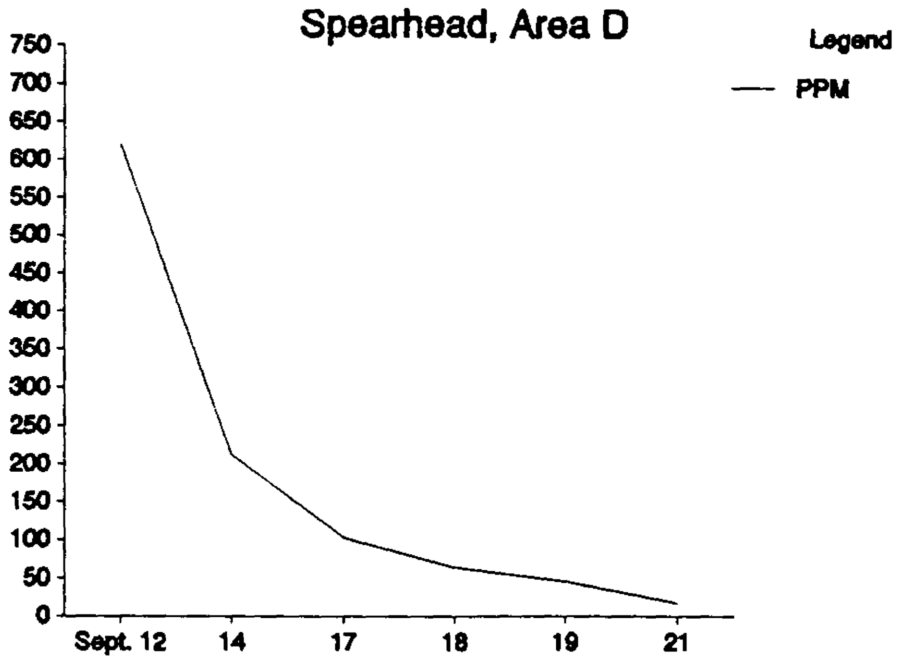


Figure 44. Graphs illustrating changes in chloride levels during electrolytic reduction.

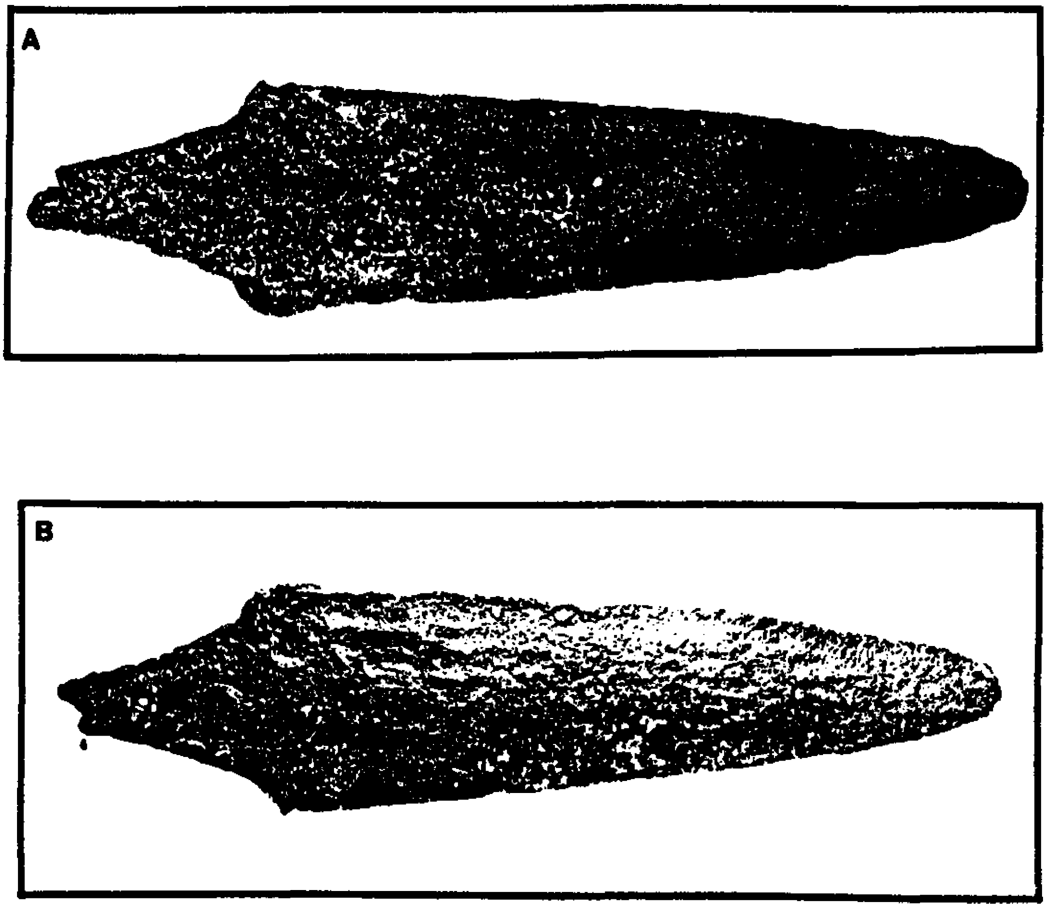


Figure 45. Before (A) and after (B) electrolytic reduction of a bronze spearhead from Area D. Length: 16 cm.

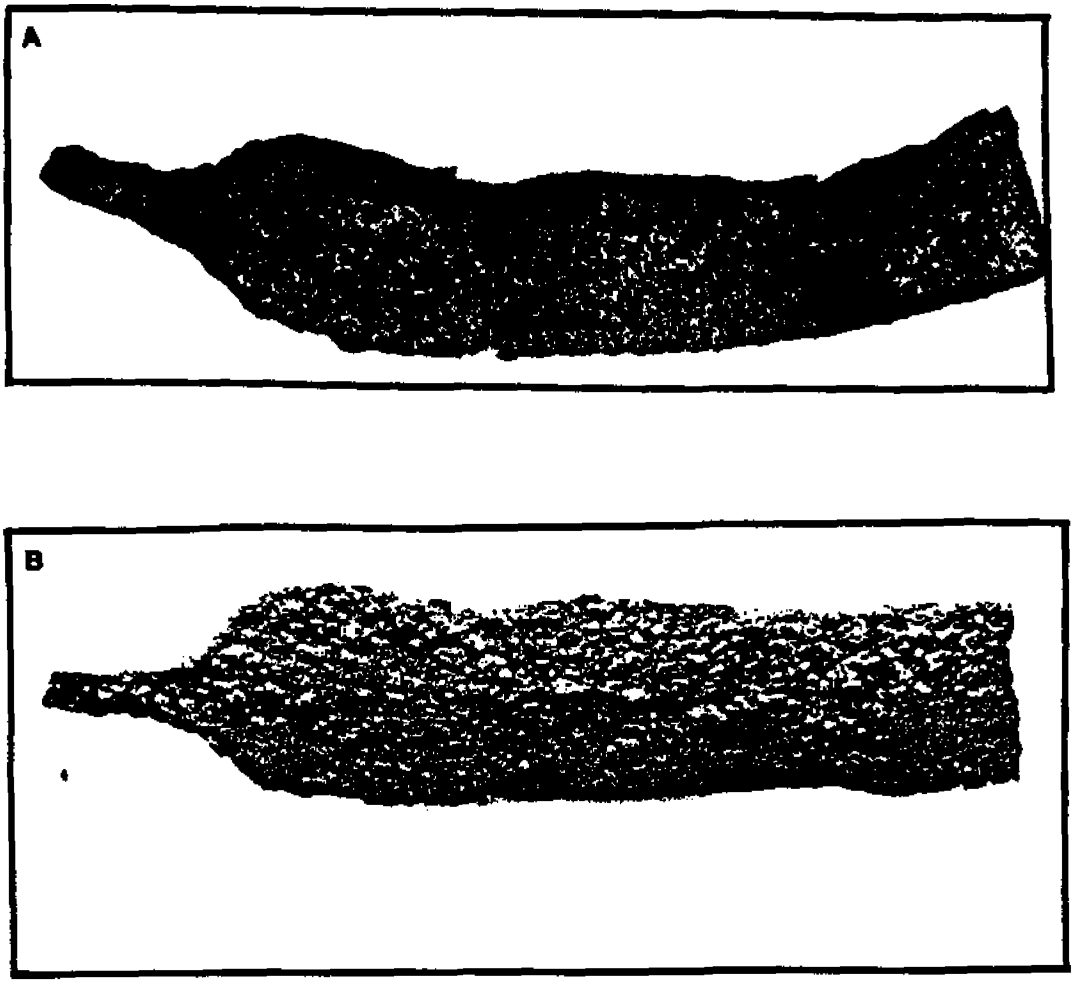


Figure 46. Before (A) and after (B) electrolytic reduction of a bronze spearhead with bent tip from Area O. Length: 14 cm.

insoluble, distilled or deionized water alone cannot remove them, but if an alkaline agent is added, then the harmful chlorides will diffuse out with time.

Weisser (1987:107) advocates the use of sodium carbonate in a series of carefully monitored 5% solutions. Patches of stable, but disfiguring black cupric oxide (tenorite) can appear when using this treatment, as well as the formation of chalconatronite, a blue-green precipitate resulting from the reaction of sodium carbonate with cuprous chloride (Weisser 1987:107-108).

The other treatment, sodium sesquicarbonate, was chosen for the Tel Nami program because it removes cuprous chlorides without damaging fragile objects that require minimal handling. Sodium carbonate and bicarbonate of soda, the two ingredients that comprise sodium sesquicarbonate, are both easy to obtain in Israel in large quantities at a reasonable cost.

The sodium sesquicarbonate treatment was first proposed by Scott (1926:36), then advocated by Oddy and Hughs (1970). The treatment works by neutralizing the hydrochloric acid produced by the cuprous chlorides in the object. Hydrochloric acid has the capacity to liberate hydrogen ions in solution and replace their own hydrogen in a metal. Alkalis such as sodium, will free hydroxyl (OH) ions in solution and neutralize the free hydrogen of the hydrochloric acid (Dowman 1970:11-12). The chlorides in the solution are then removed with each successive fresh bath of solution. Bronzes treated this way tend to remain stable over time (Weisser 1987:106).

The use of sodium sesquicarbonate has its drawbacks, including the length of time is takes to remove chlorides. Angelucci et al. (1978:153) discontinued their experiments with sodium sesquicarbonate after the twenty-eighth washing. Sodium sesquicarbonate, as a double carbonate, forms a complex ion with copper, therefore preferentially removing copper from the remaining metal. This is evident by the blue color of the solution suggesting that copper ions are going into solution. MacLeod reports that a 5% solution removes chloride ions at an initial rate of five times to that of a 1% solution, yet the loss of copper is greater. In experimenting with copper sheathing tacks, MacLeod found that while 1007 mg of chloride were removed, over 300 mg of copper were lost (1987:30). While these findings are instructive, the loss of copper is probably minimal when compared to the value of removing harmful chlorides.

Horie and Vint (1982:185) state that sodium sesquicarbonate produces changes in two ways. First, the surface seems to become more homogeneous and less porous after treatment. Then, after the copper corrosion products dissolve, copper salts are redeposited as small crystals of sodium copper carbonate hydrate (synthetic chalconatronite), changing the patina from green to a blue-green color, similar to the reaction with sodium carbonate reported by Weisser (1987:107-108). While the patina can change color, often it is enhanced, becoming a more vivid blue-green.

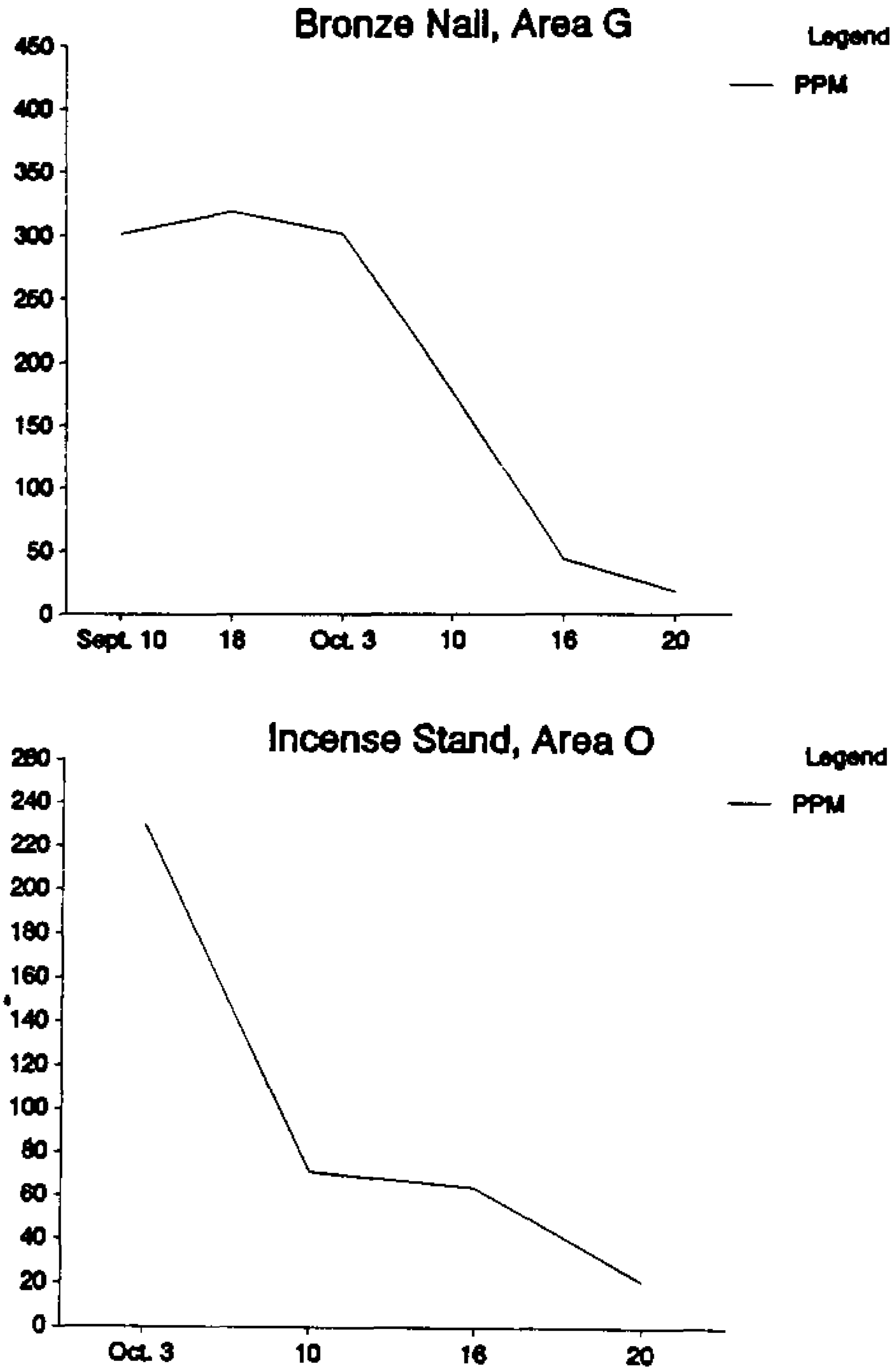
No deleterious changes were observed for any of the Tel Nami bronzes, and further studies of chalconantronite on archaeological metals are necessary in order to determine its overall long-term effects (Weisser 1987:108). Also, prolonged soaking in sodium sesquicarbonate, for a year or more may be excessive and pose a problem for the safety of the artifact (Weisser 1975:210). None of the artifacts from the Tel

Nami project required soaking for that long, nor would this treatment have been considered if this were the case. This is also a reminder that no treatment is ideal for stabilizing bronze, and that all established treatments should be used with great caution and careful monitoring.

The Tel Nami bronzes that were treated with sodium sesquicarbonate were highly mineralized and fragile, or had decorative elements or a desirable patina. The first baths consisted of 5% solutions of sodium sesquicarbonate in tap water, with the final baths in deionized water. Chloride levels were checked and recorded once a week by means of the mercuric nitrate test. The baths were changed on a weekly basis. The length of treatment varied for each object, ranging from one to five months. All treatments were continued until the chloride levels peaked, then levelled out to 35 parts per million (ppm) or less.

It has been shown that the chloride concentration is linearly dependent on the square root of the treatment time whereby the chloride levels can be plotted. The plots are characterized by a rise in chloride levels until a plateau is reached. As the baths are changed, the chlorides diffuse out at a slower rate until the gradient slopes downward with the eventual elimination of chlorides (Figure 47). The rate of chloride ion release is controlled by the rate of diffusion through the adherent cuprous oxide layer. This is in turn controlled by patina thickness and defects in the copper oxide film (MacLeod 1987:26-28).

Another treatment, the application of Benzotrialzole (BTA) was used in the Tel Nami conservation program, following several rinsings in deionized water and



Bronze Nail, Area G

Incense Stand, Area O

Figure 47. Graphs illustrating changes in chloride levels for the sodium sesquicarbonate treatment.

degreasing in acetone. Benzotrialzole can be applied either through vacuum impregnation or by soaking the object in a bath of deionized water or methanol with BTA for several days. Solvent and deionized baths were used in the Tel Nami program.

Benzotrialzole, $C_6H_5N_3$ (BTA), was first used by Madsen (1967:163-166) as a corrosion inhibitor for treating artifacts. Walker (1979) has since advocated its general use for archaeological conservation. The use of BTA is now standard practice in the treatment of cupreous metal objects. When BTA is in contact with a cupreous metal surface, it forms a thin, insoluble, chemically-bonded complex on the surface of the metal. Precipitation of this insoluble complex over the cuprous chloride forms a barrier against any moisture that could activate the cuprous chlorides responsible for bronze disease. Madsen (1985:19) states that the film formed by BTA is similar to the initial passivating film of copper alloys. The only drawback to BTA is a suspected toxicity (Oddy 1972:135). Because BTA has the potential for being a carcinogen, care should be taken in its handling by the use of gloves and goggles.

The final step in the stabilization process, following the BTA treatment and dehydration by a solvent, is applying a sealant. For the Tel Nami bronzes, a 10% solution of Acryloid B-72 in acetone or toluene with the addition of BTA, was used. Also known as Paraloid B-72, this acrylic resin is a copolymer of ethyl methacrylate and methyl acrylate soluble in acetone and toluene (Singley 1988:90), and is available commercially as Krylon 1301 in a spray can.

Reconstruction and Gap Filling

There is occasion to warrant some amount of reconstruction when it prevents further breakage or damage to an object. Reconstruction can also be instructional, so that an object may be better understood and recorded. For example, epoxy casts of artifacts are a form of reconstruction. Finally, reconstruction may be necessary to hold an object together for storage or display purposes (Cronyn 1990:90).

One of the basic tenets of conservation is the concept of reversibility. Any treatment applied should be reversible so that the option to retreat is always open (Hamilton 1976:2), however, this tenet cannot be adhered to in every instance.

For metals, Acryloid B-72, used as an adhesive is sometimes helpful, although it has been found that only epoxy resins have the necessary strength for gap filling requirements. While epoxies are not reversible, they can be softened with a solvent such as toluene.

Payton (1987:44) reports good results from applying Araldite epoxy resin mixed with graphite powder to hairline cracks in a silver bracelet found on the Ulu Burun Shipwreck. This repair now supports the surface of the bracelet while giving it a consolidated appearance.

A similar approach was taken for a small strainer from Area O (Figure 48), and small knife (Figure 49) also from Area O, similar to one identified by Lakovidis (1982:215, Figure 10A) as Mycenaean. Two heavily corroded cracked or broken bowls were repaired with Devcon, an epoxy resin similar to Araldite (Figures 50 and 51). The round-bottomed bowl, mentioned previously, had been in sixteen pieces.

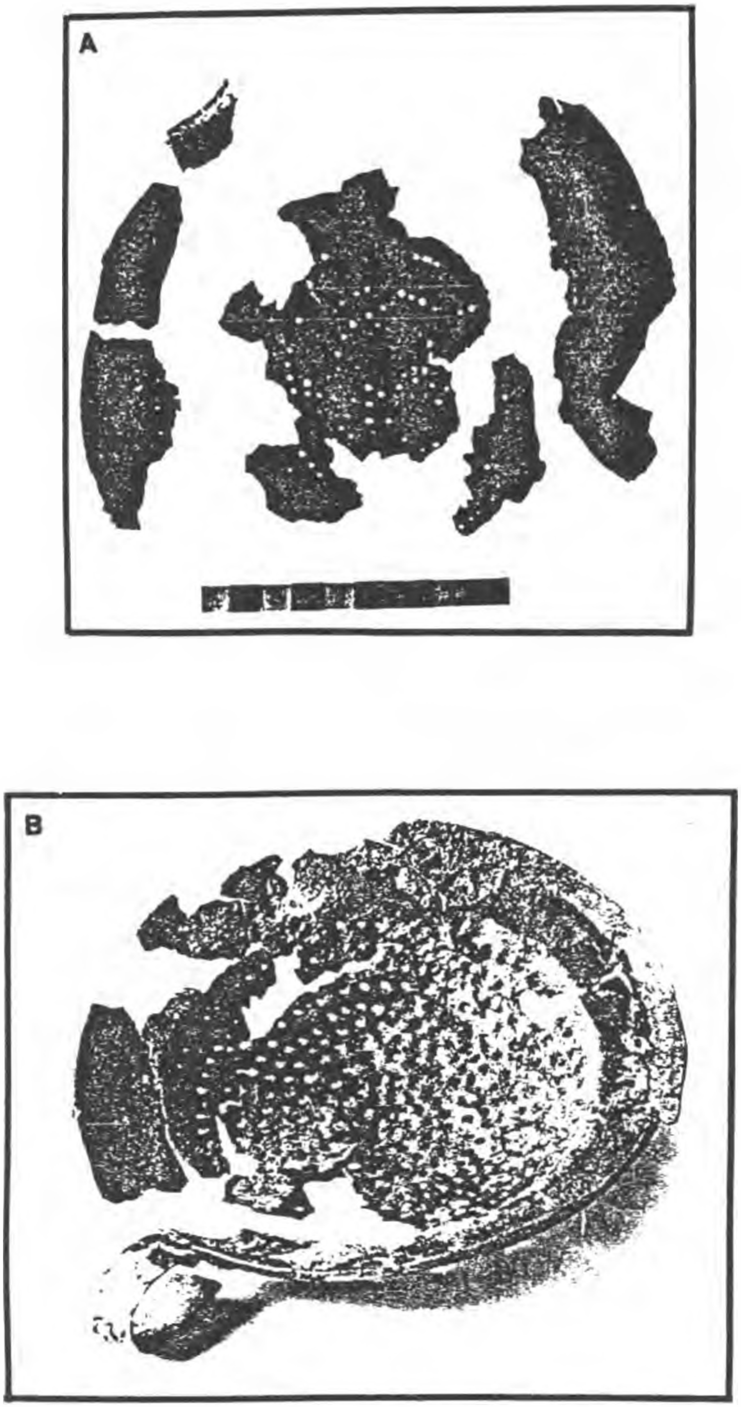


Figure 48. Before (A) and after (B) reconstruction of a bronze strainer from Area O.

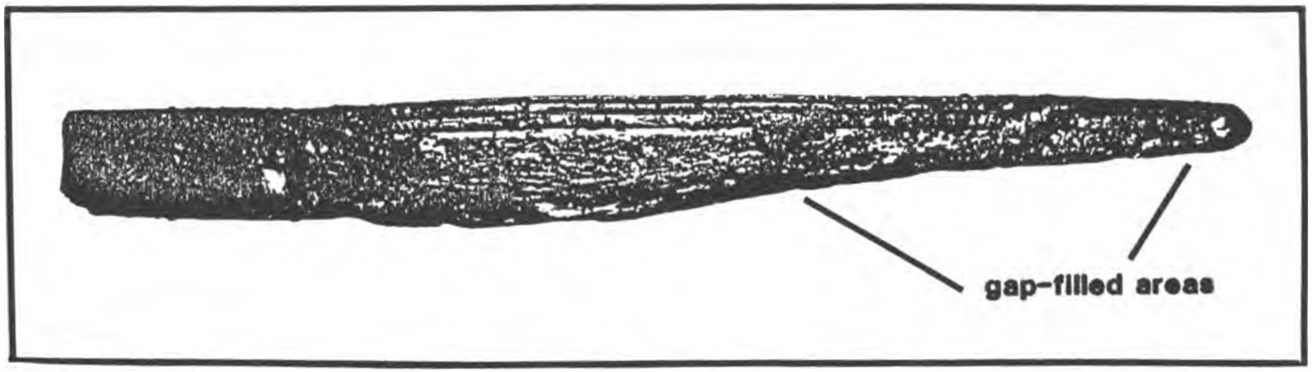


Figure 49. Small knife from Area O with repaired bottom sections.

Length: 16.5 cm.

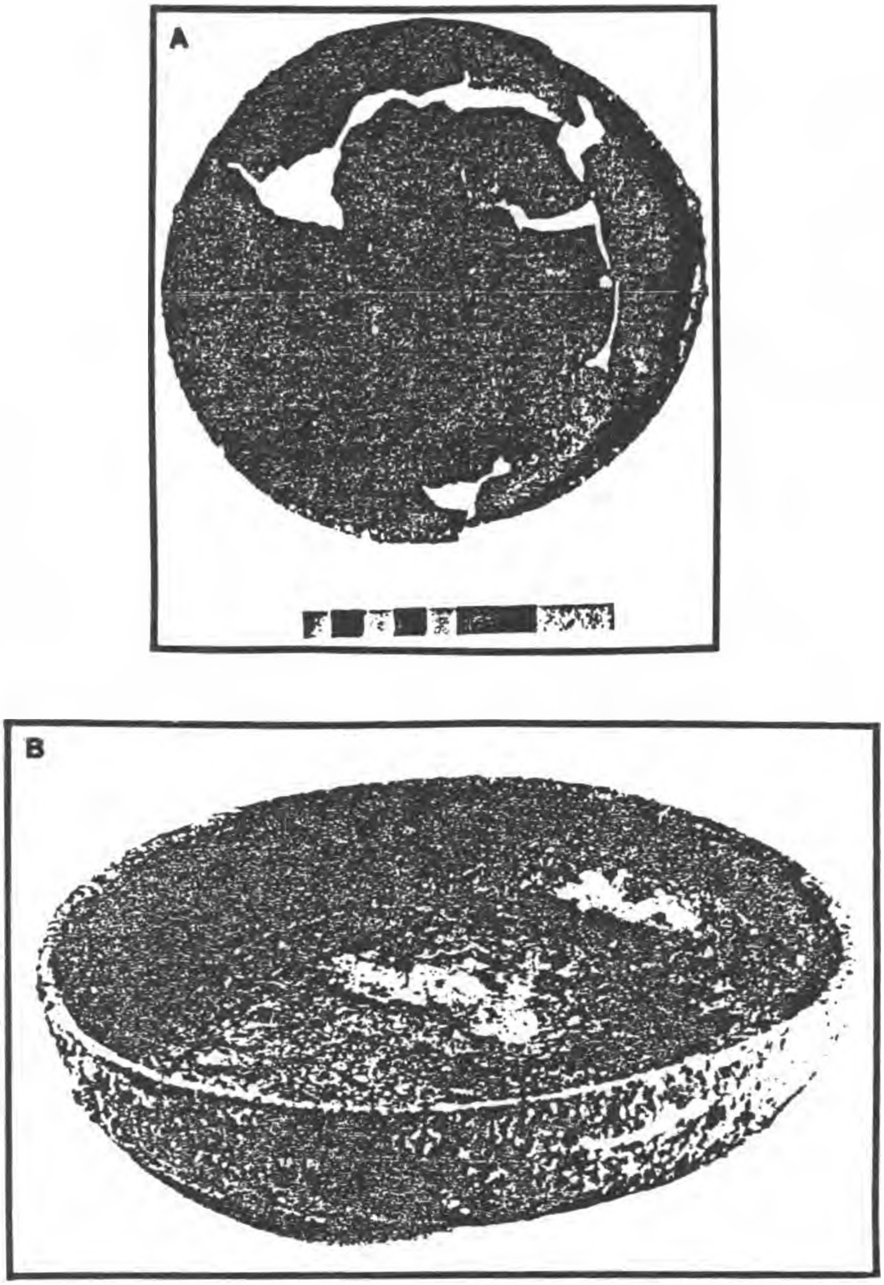


Figure 50. Before (A) and after (B) reconstruction of a cracked and broken bowl from Area O.

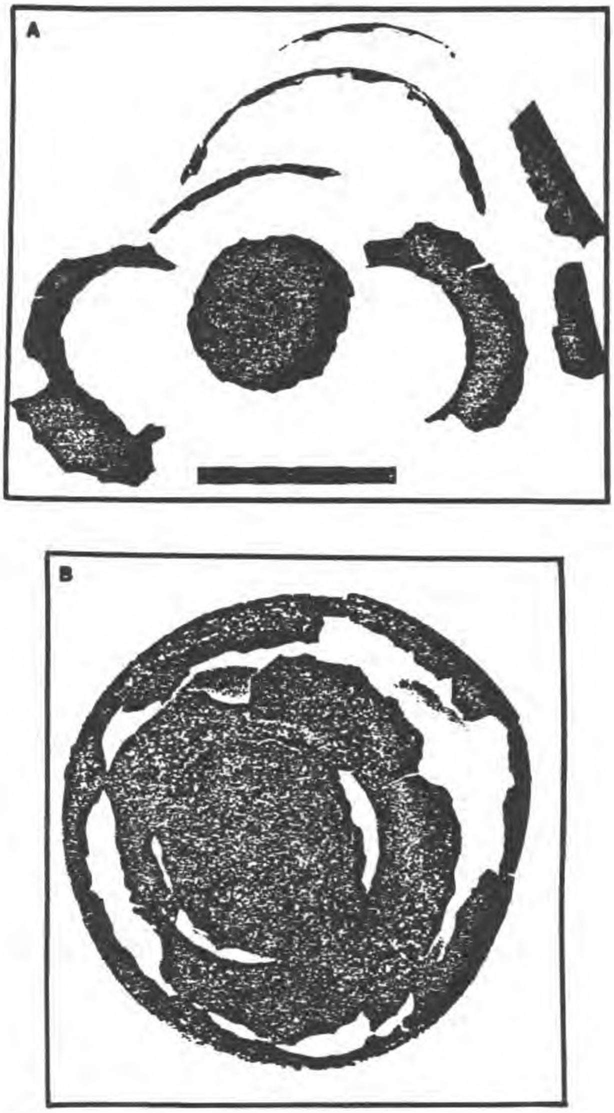


Figure 51. Before and after reconstruction of a bowl from Area O.

16 cm across.

These repairs allowed for restoring their former shape.

Implications of the Study

Archaeological conservation not only performs the valuable service of stabilizing and preserving an artifact, it also can reveal important diagnostic information pertaining to ancient technology or even the intended function of an object. Jedrzejewska (1976) discovered engraved scale armor on the backside of a statue of Amon that was previously obscured by corrosion products. She also noted that the statue was made of composite parts. Interestingly, the hands and feet of this genre of composite New Kingdom statue resemble one hand and foot found at Tel Nami, probably scrap metal pieces (Artzy 1989:10) (Figure 52).

The conservation of the Tel Nami bronzes resulted in new information in some cases. Both mail armor scale plates were unidentifiable in situ, since they were badly corroded and broken in small pieces. One was found in Area G, on the top of the tell, and the other in Area 0, in a grave. After soaking them in sodium sesquicarbonate solution for approximately one week, Dr. Artzy and I noticed small holes appearing that were previously covered in corrosion products. It was then determined that these were mail armor scale plates. This discovery is exciting, for few examples exist from the archaeological record for the Late Bronze Age Mediterranean. Perhaps leather or metal passed through the holes to secure the mail piece to the armor breast or back plate (Figure 53).

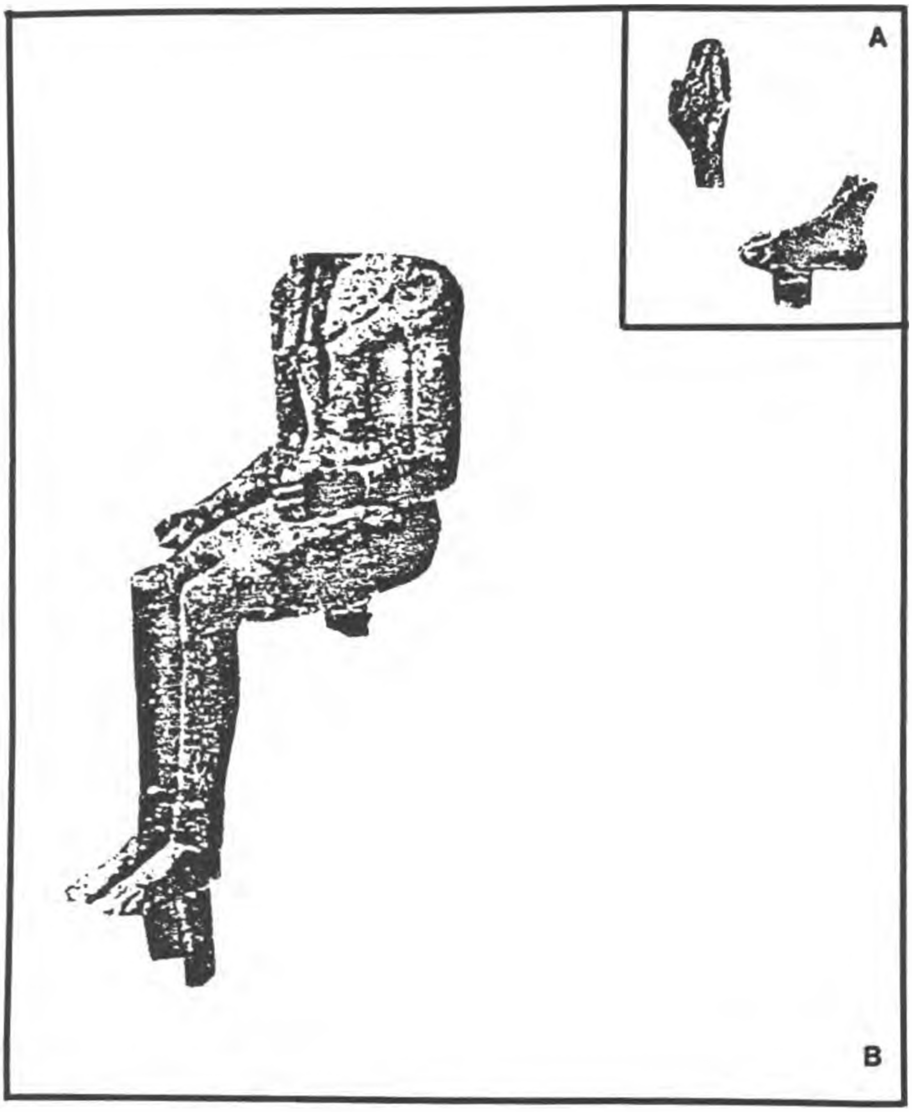


Figure 52. Hand and foot scrap metal pieces from Area D1.

Length of hand: 3 cm. Length of foot: 1.8 cm.

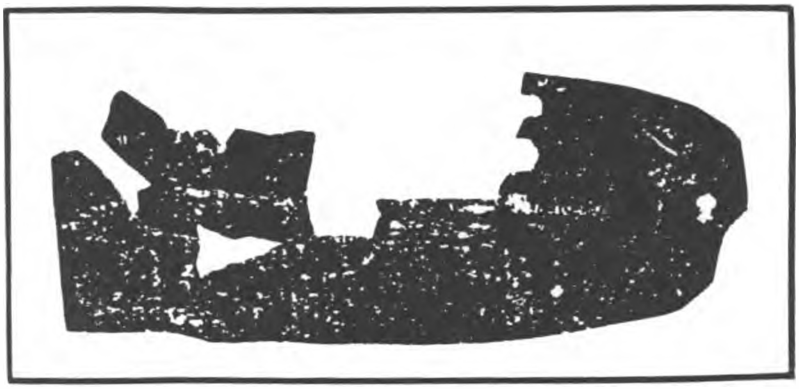


Figure 53. Scale plate mail armor from Area O. Length: 6 cm.

Another discovery was made following the cleaning of an unidentifiable object recovered from Area G. Due to its unusual shape, it was difficult to determine what the object was, particularly because it was obliterated by calcareous deposits. Following electrolysis, the details could be clearly seen on the artifact, indicating that it was a piece of scrap metal. This piece belongs to the lower half of a Cypriot tripod, as seen in Catling (1964:191) (Figure 54). This again fits the picture of a maritime scrap metal trade during the Late Bronze Age, and possibly evidence for metalworking in the temple area of Area G at Tel Nami (Artzy, personal communication).

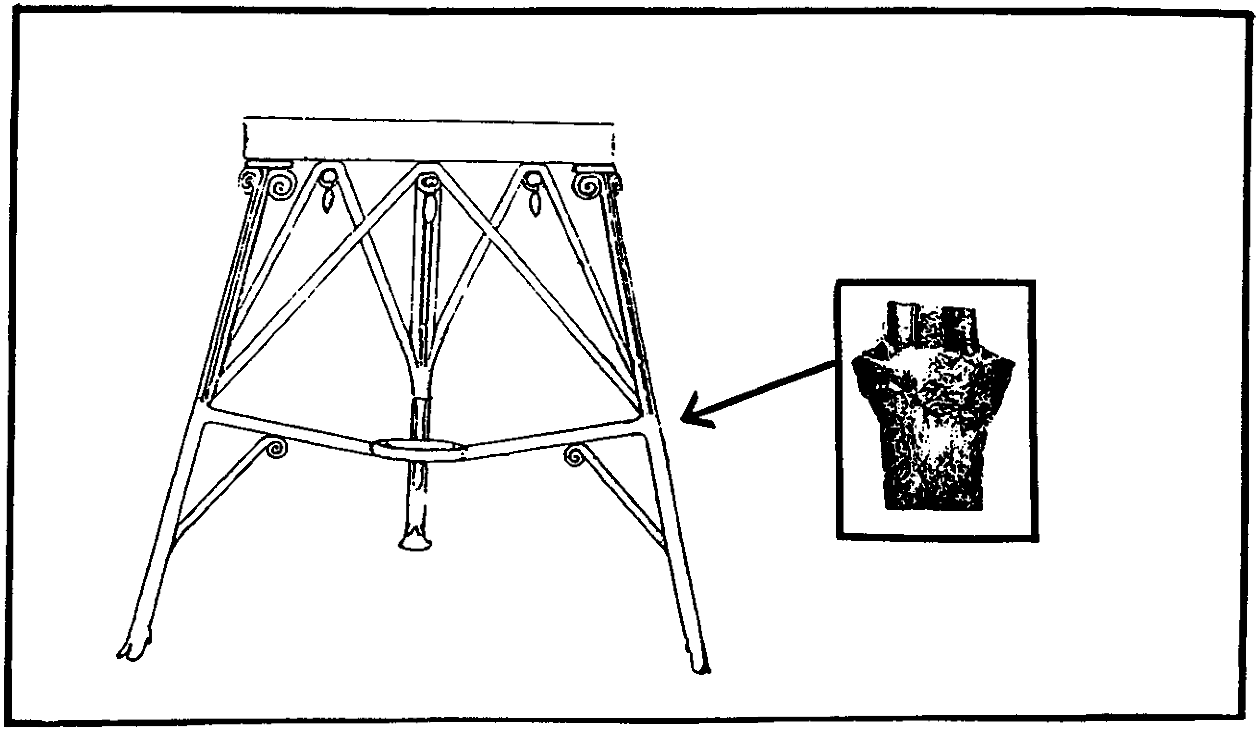


Figure 54. Section from a Cypriot bronze tripod stand (after Catling 1964:191).

CHAPTER IV

CONCLUSION

The conservation of the Tel Nami bronzes has led to an investigation into the factors contributing to in-situ corrosion processes. It has been shown that the micro-environment at Tel Nami, is complex, combining conditions found at both land and underwater sites.

As the artifacts themselves have been subjected to long periods of seawater inundation or zonal splash and sea spray activity, it would be expected that a substantial amount of deterioration would occur over time. Yet, this is largely not the case. Most of the bronze artifacts have been discovered in good condition. The conservation methods chosen for this program were based on twenty years of research and reported results in the field, along with the author's own preparation and experimentation. Removal of cuprous chloride was the main objective in designing a treatment program.

From this investigation into the corrosion and conservation of ancient bronze, two conclusions can be drawn. First, the micro-environment at Tel Nami is corrosive to metal artifacts, due to the presence of chlorides. It was found that objects excavated from the dense clay matrix were consistently more corroded than artifacts recovered from the sandy matrix on the site, so that salt-saturated clay can be considered to be more corrosive than sand at a marine coastal site. The dense clay would be more anerobic, and this would harbor sulphate reducing bacteria.

Secondly, it was found that cast objects suffered the least from corrosion, while artifacts that had been cold-worked were substantially more damaged by stress corrosion cracking and pitting. This is in agreement with Tylecote's study where cast objects found in British sites were more corrosion-resistant (1979:345). This also bears out the observation that cold-working does reduce metal homogeneity and creates anodic stress area that increase the corrosion rate.

Archaeological conservation is a unique area within the field of conservation which has its own problems and considerations. Therefore, this study confirms my belief that archaeological conservation should be practiced by archaeologists who have been trained in conservation or by conservators who possess a strong background in archaeology and a history of technology.

Price (1984:1) states that conservation needs for an excavation should be anticipated during the initial stages of planning, with actual conservation beginning in the field. For these reasons, archaeological conservators are equipped to anticipate these needs, based on their experience and training. This would hopefully contribute to an ongoing improvement of conservation standards for excavated material, since the ultimate goal is to recover the maximum amount of information and preserve artifacts for future analysis.

Practicing archaeological conservation includes several aspects. The main consideration should always be preservation of the artifact, which overrides aesthetic considerations. For example, a patina may be sacrificed for the sake of chloride removal.

A second consideration is retaining the diagnostic attributes of the artifact. Based on the results from this conservation program, both electrolytic reduction and sodium sesquicarbonate treatments were valuable in revealing important diagnostic information about some of the objects under study. In the same vein, when objects were found with particular attributes, they were carefully treated to avoid changing or losing this information. For example, a spearhead from Area O was found with the tip purposely bent back. In this case, it is not the conservator's job to change this, but rather record this information since it may relate to a recognized cultural practice. Burned ceramics also tell a story, and it would be unethical for the conservator to clean the blackened areas off.

Diagnostic attributes also extend to sometimes preserving corrosion crusts. Preparing samples from these crusts for analysis can be beneficial in understanding the type of corrosion involved. For example, there is some question as to whether sulphate-reducing bacteria is creating corrosive conditions at Tel Nami. Future analysis of corrosion crusts may shed some light on this possibility.

Some of the artifacts were heavily mineralized so that little could be done with them except treatment for chloride removal and epoxy repairs to protect them from further breakage. As mentioned previously, epoxy resins are not reversible. Reversibility is one of the tenets of conservation, however, experience from this study has shown that adhering to this ideal is not always possible. Pye and Cronyn (1987:355-356) state than even the simple cleaning of an object is an irreversible act. In truth, irreversibility is unavoidable in most cases.

A final consideration worth mentioning is the importance of storage following the completion of any conservation treatment. Acid-free tissue paper, cotton bags and silica gel all contribute to deterring moisture which can activate corrosion. In Israel, the humidity can be relatively high near the coast, so that proper storage of metal objects is crucial to prevent further corrosion from taking place. The Tel Nami bronzes have been sealed in bags and stored in boxes in a cool, dry place. This hopefully will promote continued preservation.

In conclusion, the conservation of archaeological materials involves more than just laboratory procedure. Rather, it is a philosophy encompassing an understanding of the archaeological environment and the deterioration processes that affect material culture. Working in a foreign setting provides the opportunity to implement resourceful solutions both in the field and in the laboratory. It also creates a forum for sharing and exchanging ideas on an international level that leads to a greater understanding of the goals and objectives of archaeological conservation.

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