

CHAPTER 3

Man Courts Lead

Metallurgy and Alloys

*Thou are a soul in bliss;
but I am bound upon a wheel of fire,
that mine own tears do scald like molten lead.*

Shakespeare *King Lear*

Part One: History, Art, and Technology

Chapter One demonstrates that lead is more abundant than many other toxic metals and that the bodies of lead ore lay close to developing agrarian societies. It was further shown that lead was married to silver ore. Chapter Two demonstrates that dispersion of lead began with the advent of large scale silver mining for coinage. Over time, labor, fuel, and technical difficulties were solved to extract and refine lead and silver. What was the extracted lead used for, apart from purifying silver and the occasional use of lead for coins and tokens?

While the ancients did make pure lead objects (lead tumblers have been found in graves from 3100 B.C.) they also found lead useful in other ways, particularly in the formation of bronzes. This chapter will examine the following questions:

1. What is it about lead that made it a useful manufacturing metal?
2. Why was lead often added as an alloying agent in bronzes?
3. Why was lead in other alloys, particularly in metal sulfides?

PURE LEAD METAL OBJECTS

Lead as Sculpture and Lead as Plastic

Lead's ease of deformation resulted in its early use in the manufacture of objects. Figurines of pure lead date from before 3000 B.C. The idol shown in Figure 3.1 is from southern Lebanon and dates back approximately to 2000 B.C. The idol is too complex to have been manufactured by open or closed molds; it

must have been made by a lost wax method (Krysko, 1979, Figure 89). Material of a similar date are the cannel coal and lead beads dated to 2100-1600 B.C. found in Scotland (Davis et al., 1994; Hunter and Davis, 1994). Chinese lead objects dating to an early period were ritual burial vessels. An example is the lead Chueh of approximately 1000 B.C. (Figure 3.2). The Chueh does not have the appearance of pure lead because of the cerusite ($PbCO_3$) coating occurring after burial (Gettens, 1969, Figure 233). A lead figure from the Greek main lands (Laconia) dates to 1400 to 1300 B.C. (Figure 3.3) (Pedley, 1993, p. 98).

Once metallurgy of copper and bronze was mastered, pure lead apparently was relegated to use as a cheap, disposable material, rather like plastic today. Many of the surviving Western lead objects are trinkets associated with the temple trade. Figure 3.4 shows a lead amphora shaped like a wine vessel from 400 B.C. Greece. It was likely purchased as a devotional or commemorative object at the temple. Figure 3.5 shows a lead frame to a 2 inch Roman burial mirror. Figures 3.6 and 3.7 show lead die for gaming and a decorative lead head, the latter purportedly from an English villa.

Lead was also used instead of wax for sealing important documents. Figure 3.8 shows the Papal Bulle (seal) of Pope Gregory VIII (1227-41 A.D.). On the reverse are stamped the heads of St. Peter and St. Paul. The use of wax on these Bulls was supplanted by lead about 615 A.D. Lead was used in other types of seals, including kosher seals for poultry used in Europe in the 1700s (Figure 3.9).



Figure 3.1: Lebanese lead Idol, 2000 B.C. from Staatliche Museum Preussische Kulturebesitz, Museum für Vor und Frühgeschichte, Berlin. (Krysko)

Lead continued to occupy the trinket niche right up to its displacement by plastics. Figure 3.10 shows “action figures” from the 1950s made of lead. Lead was also used as the tinsel for Christmas trees (Figure 3.11).

Lead Sculptures Revival

Lead as a true sculptural material experienced a minor revival in Europe in the 1600s, heralded by the building of fountains in the Garden of Versailles, France, by Jean Baptiste Tuby. A good example is the “Chariot of Apollo” (1669) built for Louis XIV. It shows the sun king breaking forth upon the day (Krysko, 1979, Figure 166) (Figure 3.12). (It was a joke, perhaps, or hyperbole, since Louis XIV was known as the sun king.) The work at Versailles inspired many other artists of that time period in Europe. The



Figure 3.2: Cheuh, approximately 2000 B.C. with a crust of lead carbonate. Gettens, 1969, Fig. 233

notable sculptor George Raphael Donner (1693-1741) created his most famous lead work for the Vienna City Council in 1737. It was the central market place fountain, the Providentia Fountain (Figure 3.13). Because pieces were chopped off for ammunition, the statue was removed (Krysko, 1979, Figure 180). (The next section will pick up this theme of lead as projectiles.)

A lesser known worker in lead sculpture was René Fremín. He worked for the King of Spain. The King of Spain followed the King of France in the craze for large lead garden ornaments. Some do not appear to be lead because they are painted white (1989). Lead became very popular for garden sculptures in England (Figure 3.14) during this time. The main lead work factory was that of the Dutchman Jan van Nost. (Maden and Neubert-Maden, 1997) The main garden sculptor was Andrew Carpenter. Two of his more



Figure 3.3: Mycenaean lead figure: 1400 to 1300 B.C. In John Griffiths Pedley, *Greek Art and Archaeology*, Harry N. Abrams, 1993. National Museum of Athens



Figure 3.4: Ancient Greek amphora about 1 inch high. (Author's collection)



Figure 3.5: Lead Roman mirror mount approximately 2 inches high. (Author's Collection)

famous of his works are *Hercules Slaying the Hydra*

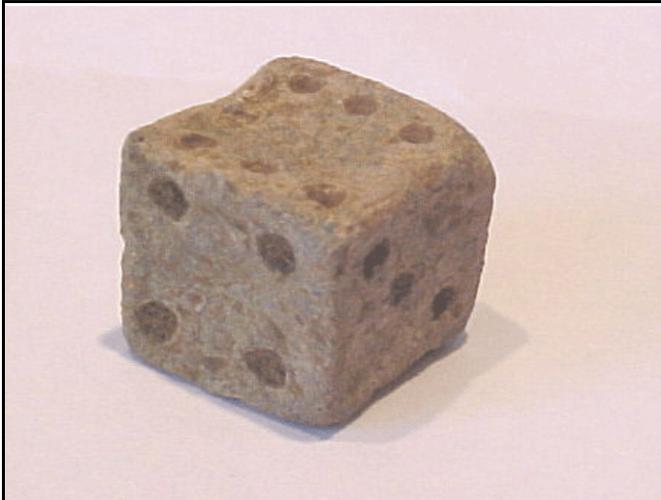


Figure 3.6: Roman lead gaming die. . (Author's collection)



Figure 3.7: Roman head relief in lead, purportedly from a Roman villa in England dating from the 2-3 century A.D. Size is 1.5 inches. ((Author's Collection)



Figure 3.8: Pope Gregory VIII (1227-41 A.D.) Papal lead seal. (Author's collection)



Figure 3.9. A lead seal from Europe, 1700s, used to indicate that the attached product was kosher. (Author's collection).



Figure 3.10: Toy lead figures from the 1950s. (Courtesy of Al B. Benson, III).

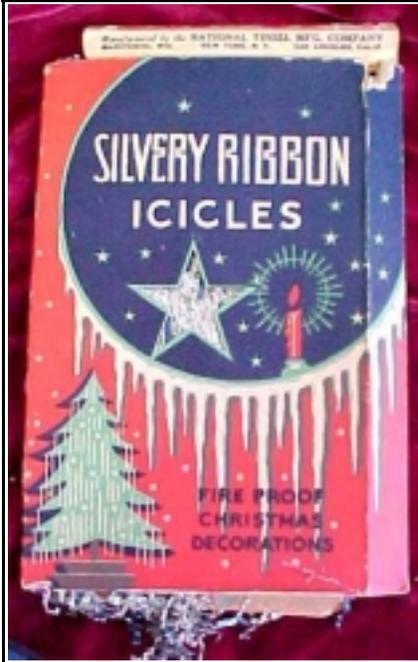


Figure 3.11: Lead used as tinsel on Christmas trees. (Author's collection.)



Figure 3.12: “Chariot of Apollo” sculpture by Jean Baptiste Tuby (1669) at Garden of Versailles, France. (Krysko, 1979, Figure 166).

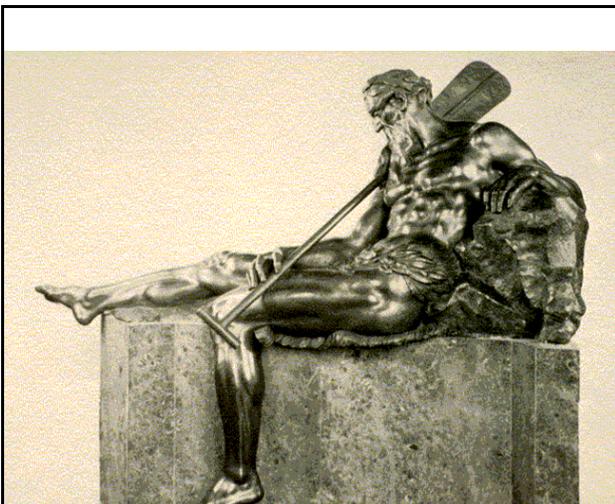


Figure 3.13: George Raphael Donner, Providentia Fountain, Vienna City (1737) in the History Museum of Vienna State (Krysko, 1979, Figure 180.)

(1739) and *Fame Riding Pegasus* (Weaver, 1909).

Other early sculptors using lead are Johann Baptist Hagenauer (1732-1810) and George Gilbert

Scott. Hagenauer in 1759 produced *Chained Prometheus*. One art commentator waxed poetic over this particular statue: “There was a deliberate choice of lead to interpret significance of the subject. The intense pain and long suffering of Prometheus are immediately impressive in the dull grey lead. It’s patina is non-reflective. By using lead Hagenauer was able to achieve the desired somber effect”

George Gilbert Scott was the designer of the Albert Memorial in London’s Kensington Gardens. Albert Francis Charles Augustus Emmanuel of Saxe-Coburg-Gotha married Queen Victoria in 1840 and died of typhoid in 1861. This memorial was constructed from 1863 to 1876 and consists of a lead panel inset with colored glass and hard stones. After a 2,000 pound piece of lead fell the monument was closed, then reopened in 1998.

A famous modern sculptor working with lead as a medium is Henry Moore. He produced a series of figures in lead during the 1930s, including Figure 3.15, *Stringed Mother and Child* (1938) (Mitchinson and Stallabrass, 1991). Lesser known is the sculptor Antony Gormley. Art critic Michael Archer described Gormley’s use of lead in a 1984 exhibition: “*Gormley*



Figure 3.14: Victorian Garden Stature. The Hazelby Garden. Designed so the grey contrasts with the green. From *The English Formal Garden*, Maden and Neubert-Maden, 1997.

has adopted lead as the appropriate material in which to render the human form. The properties of lead make it an emblem of the history of our attempt to comprehend matter. It's structural proximity to gold gives it alchemical significance and yet its denseness and resistance to penetration ensures its continuing usefulness in a nuclear age" (Archer, 1984).

Our last example of a lead sculptor is Franz Xaver Messerschmidt (1736-1783 A.D.). In 1769, he was appointed instructor at the Vienna Art Academy. His application for a promotion three years later was turned down because of his paranoid tendencies. In 1770 he suffered a mental breakdown and gave up on art. When he died several lead casts, including one of his own face titled *Peevish Old Man* (Figure 3.16), were found (Krysko, 1979, Figure 188). It has been suggested that his breakdown and subsequent withdrawal from work were due to symptoms of lead poisoning (Moffitt, 1988). A contemporary describes his visit with "M" in the following way:

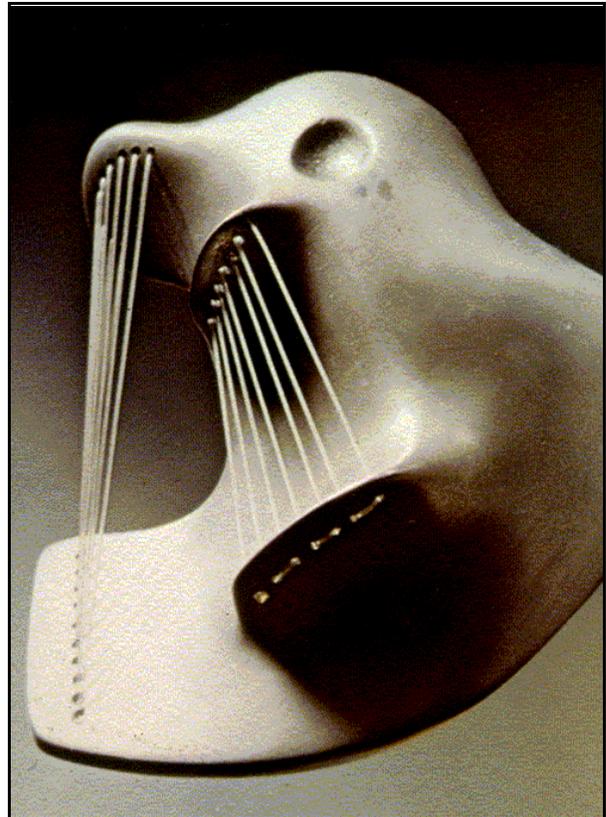


Figure 3.15: Henry Moore *Stringed Mother and Child* (1938). From Mutchinson and Stallabrass, 1991).

I noticed that M. glanced at these busts briefly with fixed eyes and quickly turned his head away. Thereupon I asked him rather cautiously what these busts represented. M. seems reluctant to come forth with an explanation....and his otherwise vivid eyes turned glassy when he finally answered in broken words: "That one" [referring to the "Demon"] had pinched him, M., and he in turn pinched the Demon and these figures were the result of it. [And he added,] "I thought, at last, I will subdue you, but he [the Demon] nearly died in this effort.' From what he said, I realized that these caricatures of human faces were actually the figures in which the deluded fantasy of M. saw the Demons of Proportion.

-Friedrich Nicolai, 1781, in a letter describing his visit to M.'s studio where he shut himself away with his lead figures.

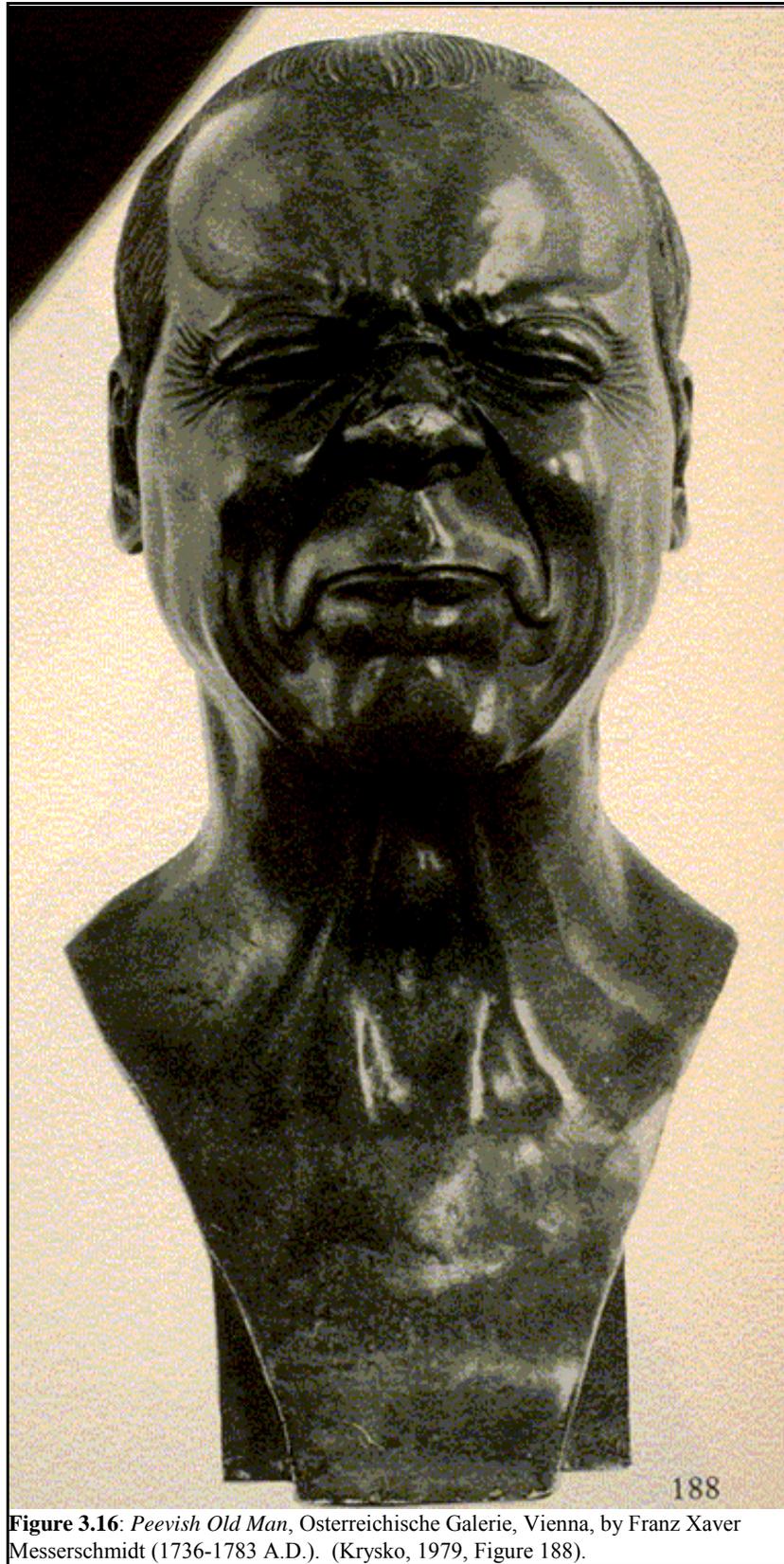


Figure 3.16: *Peevish Old Man*, Österreichische Galerie, Vienna, by Franz Xaver Messerschmidt (1736-1783 A.D.). (Krysko, 1979, Figure 188).

Projectiles

Many public statues made of lead disappeared during periods of war. Lead has a long history associated with warfare. Xenophon, a pupil and friend of Socrates (434-355 B.C.) of Greece extolled the aim of a Rhodian slinger who could cast a lead weight 2 times further than Persians manned with stones. The lead weights used by the Greeks were specially manufactured for warfare. They were almond shaped bullets about 5 cm long, 2.5 cm wide and weighing 35 g, tipped with iron. They were cast in a clay mold and were often inscribed with insults to the enemy (Nriagu, 1983, p. 261). The main advantage that they gave Greeks over the Persians was the ability to mold and shape the lead into aerodynamically favorable shapes.

Figure 3.17 shows a slingshot bullet attributed to the Battle of Monde, Spain from the legions of Pompeii and Julius Caesar. The oval shape is similar to that of a bird's body and increases aerodynamic flow.

The European medieval text *Mappae Clavicæ* (900 A.D.), a compilation of words of wisdom from the ancient Greeks, describes the use of lead arrows for setting things on fire

264. The lead arrow, for setting on fire

Melt lead once, twice, or three times, and clean it of all dross, and leave it until it is collected.... After this bring up a tray, properly pound the lead in it, soak it with vinegar, then take the scum that it gives out and dip the arrow in it. Sharpen the arrow with this scum on [a plate of] lead, as on a whetstone, until it is shining bright; the arrow itself will now be thoroughly coated with lead (Smith and Hawthorne, 1974).

Other projectiles were the lead bullet launched by the transitional cross bow, followed by the gun



Figure 3.17: An oval slingshot bullet. attributed to the Battle of Monde, Spain, legions of Pompeii and Julius Caesar. (Author's collection).

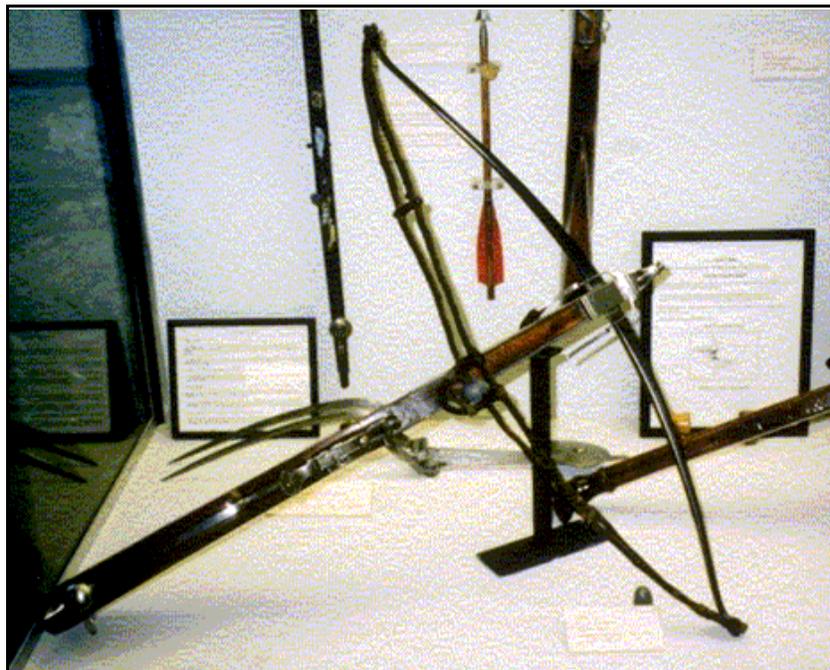


Figure 3.18: Crossbow: Warwick Castle launches not an arrow but a bullet. (Author).

bullet itself (Figures 3.18, 3.19, and 3.24).

The grandchild of the lead sling shot is, of course, the lead bullet and/or cannonball propelled through a tube by the expansion of gases. The use of firepower to propel the bullet depended upon the development of gunpowder. Gunpowder is first mentioned in 850-859 A.D. in *Classified Essentials of the Tao or the True Origin of Things* by Cheng Yin.



Figure 3.19: The crossbow launches a lead bullet (Warwick Castle). (Author).



Figure 3.20: Water droplets are not spherical when attached to a some object due to surface tension. Photo by author.

Tseng Kung-Liang published three recipes for gunpowder in 1040-1049 A. D. The first shrapnel bomb was apparently produced in 1221 A.D. in China.

The first “gun”, a small cannon, was described in China in 1288 A.D. during the time period of Marco Polo’s trip (1271-1295 A.D.). By 1267 A.D., Roger

Bacon had described gunpowder in Europe (preceding publication of Marco Polo’s books in 1298 A.D.). The first use of gunpowder-driven lead projectiles in Europe occurred during the battle of Chioggia between the Genoese and Venetians in 1380 A.D. The first drawing of a portable cannon (the gun or musket) is that of Leonardo da Vinci’s wheel-lock musket dating to 1500 A.D.

Shot Towers

All of the early projectiles were created by hand or by molding. Lead shot could be produced by passing molten lead through a sieve, but the shot obtained was irregular in shape.

The manufacturing method changed dramatically in 1782 when William Watts, an English plumber, noticed that a water drop is tear shaped as it detaches from a surface and begins to fall (Figure 3.20) but becomes spherical as it falls. He thought to apply this principle to lead. The key was to allow the lead droplet to fall long enough to cool and solidify so that it did not deform on the impact of landing (Figure 3.20). He built up his house to six stories to create the first Shot Tower ever in Bristol. Lead was poured through a sieve at the top, dropped through the six floors to land in a tank of water (Rowe, 1983).

In the United States the Shot Tower industry got its start when President Jefferson imposed an embargo on imported shot in 1808. Within a year a Shot Tower was erected near Saint Louis at the town of Herculaneum by Moses Austin. The Missouri Gazette of March 1, 1809 wrote

At Herculaneum a shot manufactory is now erecting by an active and enterprising citizen of our Territory; the situation is peculiarly adapted for the purpose, having a natural tower, or rather stupendous rock, forming a precipice of about one hundred and sixty feet, having the lead mines in the neighborhood, and one of the finest harbors for vessels. We presume the proprietor (J. Macklot) will be enabled to supply the Atlantic States on such terms as will defeat competition.

By 1830 the Youle Shot Tower, Manhattan Island



Figure 3.21. A water droplet becomes spherical after detachment but can deform on impact. Source: <http://www.kapturegroup.com/photography/htmls/waterdro.html>

(Figure 3.22), was selling much of the inventory to hardware and sporting goods dealers in New York and Pennsylvania. The dealer supplied the Indian Bureau, the American Fur Trade and suppliers in the south and west.

In 1836 the St. Louis Shot Tower purchased the J. H. Alford Company and its Herculeum shot tower. A partnership was formed with John Latty in 1840 resulting in the F. Kennett and Company. At the same time the Helena Shot Tower in the Galena territory was doubling its output (Libby, 1895).

A major player in the western shot supply was Eliphalet Wickes Blatchford who was to become one of the most important civic leaders of Chicago. He served on the sanitary commission which reversed the flow of the Chicago River, he served on the Board of the Field Museum, and was the primary Trustee to the Newberry Library.

Blatchford's wealth came his ventures into

shot manufacturing and supply of lead to the U.S. government for the Civil War effort (Blatchford, 1962). He originally went into business in St. Louis in 1850 where he made bar lead sold to hunters and sportsmen. He acquired a following among this group by stamping the customer's name on each bar. Lead bullets were cast in molds to fit the unevenly manufactured guns. Pig lead of a weight of 65-75 pounds was shipped to forts or settlements close to water travel as ballast and then melted into smaller bars for trade. "B" bars were 20-25 pound size and are often found inland.

Blatchford's other notable achievement in St. Louis was to connect St. Louis to the eastern U.S. telegraph lines by carrying the wires across the Mississippi in lead pipe. In 1853 Blatchford bought out his principal competitor, the J. W. Roberts Company and invited Collins to join him in a partnership. The new firm, Blatchford and Collins had a virtual monopoly on many branches of the lead manufacturing business west of the Alleghenies. When the railroads arrived in Chicago the company opened a branch there in 1854. Blatchford eventually moved to Chicago with his new enterprise the Chicago Lead Pipe and Sheet Works located at N. Clinton Street.

Blatchford's business expanded extensively with the Civil War as he contracted with Captain John A. B. Dahlgren of the Navy Yard to supply lead wire of the exact diameter to fit automated bullet machines. He apparently processed some 12,000,000 pounds of lead worth 6.5cents/lb to the tune of \$780,000/year during the Civil War period.

When Eliphalet Wickes Blatchford opened his new shot tower in Chicago it merited notice within the community. It was mentioned in the book, *Illustrated Century*, Aug. 20, 1887.

The Big Shot-Tower. High above all the surrounding factories and dwellings, even above the tallest chimneys, standing like a sentinel over the fork of Chicago's river, may be seen what is popularly known as "Blatchford's Shot-Tower." This structure was erected in 1867, being of the usual rigid simplicity of its kind,.....over 200 feet high..... The original builder, E. W. Blatchford, has transformed that branch of his manufacture into what is known as the Chicago Shot-Tower Co., the Blatchfords still continuing to be members of the same.



Figure 3.22. Jasper Cropsey's *Youle's Shot Tower*, 1844. This is an example of the second generation of the Hudson River Valley school of art. Oil. Museum of the City of New York.
<http://www.mcny.org/Painting/pttcat16.htm>

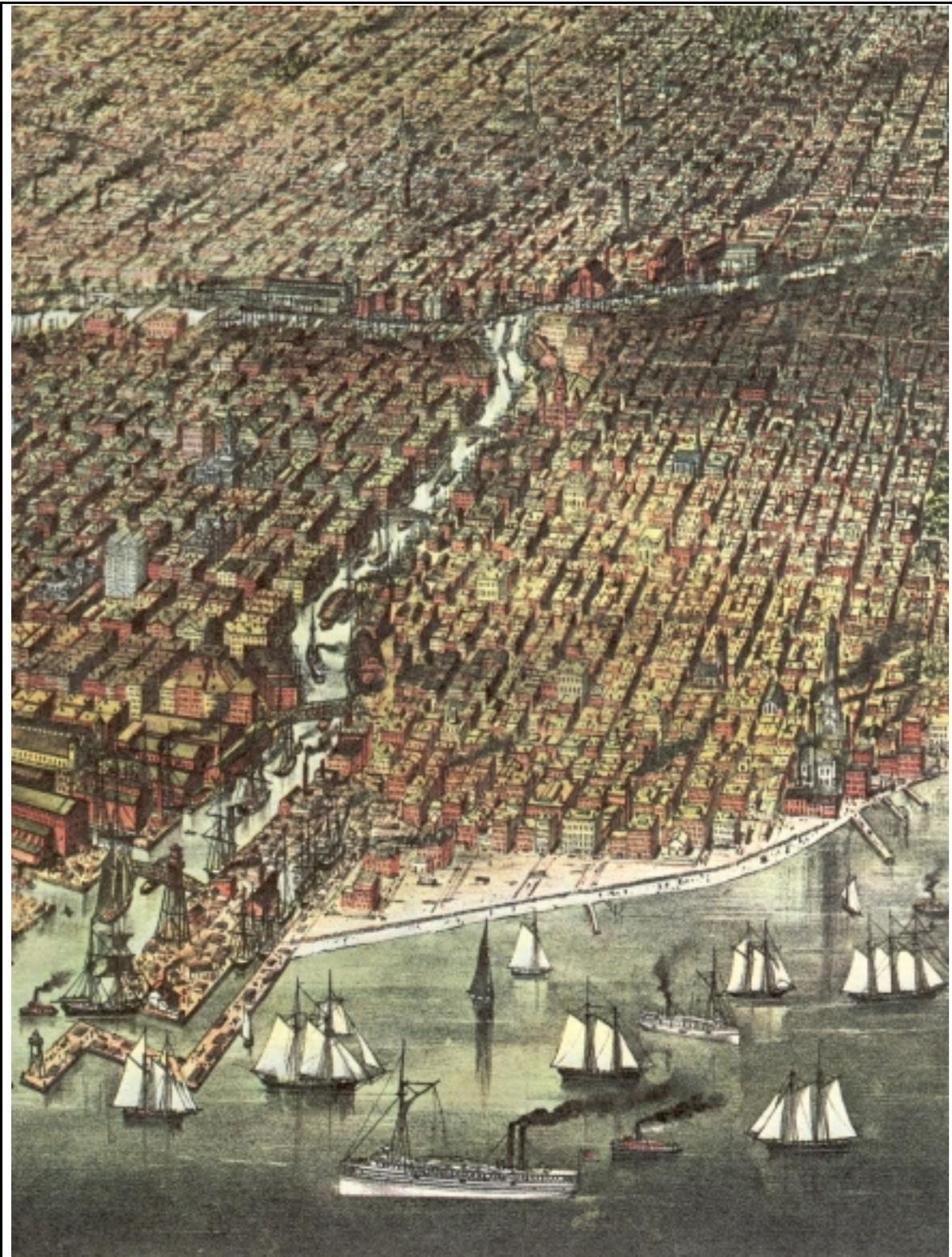


Figure 3.23 Image of Chicago from the lake. At the juncture of the two branches of the river, slightly to the right and beyond can be seen the towering Chicago Shot Tower. Currier and Ives Lithograph. The City of Chicago, 1892. Original: Amon Carter Museum of Western Art, Forth Worth, Texas.



Figure 3.24: Lead bullet mold, various 19th century bullets, and a bag for holding Dutch Boy lead shot. (Author's collection)

Figure 3.23 shows an image of the City of Chicago in 1892 in which the Chicago Shot Tower can be seen just beyond the juncture of the rivers.

Lead continues to be used in the production of projectiles (Figure 3.24). In the United States, only two sources of lead consumption increased during the last 40 years: lead acid batteries and munitions. The later category includes bullets and propellants. While the bullet or shot may kill you instantaneously, it also possible to have delayed mortality related to toxicosis from the lead shot (Cagin et al., 1978; Dillman et al., 1979).

Children have been known to chew on lead bullets and lead shot. One six year old child was found to have a blood lead level of 34 $\mu\text{g}/\text{dL}$ at the age of 6 although her blood lead level was 4 $\mu\text{g}/\text{dL}$ at the age of 1 year. Soil lead was <2 ppb and house dust lead <14 $\mu\text{g}/\text{ft}^2$. The source of lead poisoning was her habit of chewing on lead pellets from a pellet gun (Roberts et al., 1998).

Lead Weights

Lead weights have been used since lead itself was discovered. The weights are used as standards, as



Figure 3.25 A 1 ancient Greek inch plumbing bob weight shaped like a pyramid. (Author’s collection.)

plumb lines in architecture (Figure 3.25), and as sinkers in fishing. The use of lead for weights depends upon its role as the most dense of elements. A line terminating in a lead weight can be used as a plumb line to determine the vertical when constructing walls in a house. Lead can also be used to make cloth fall in a smooth way. Martha Washington’s dresses were weighted with lead at the hem line to create a good “look” (Figure 3.26). Curtains are also weighted to fall smoothly. At least one dog has been poisoned by ingesting curtain weights (Drell, 1997). There have been three cases of childhood lead poisoning by ingestion of curtain weights. Two cases were asymptomatic, but one resulted in pallor and lethargy (Mowad et al., 1998).

Lead is used as sinkers to catch fish. In this capacity, it is harmless to the user, but its improper disposal can constitute a source of danger. It has been suggested that lead weights in fishing streams are ingested directly by bottom feeding geese and raise the amount of lead in the water (see Chapter 8). Lead fishing sinkers have been implicated in at least one case

of asymptomatic childhood lead poisoning (Mowad et al., 1998).

The greatest risk of lead fishing sinkers is to wildlife, and as such several legislative bodies have banned lead sinkers (AP, 2002).

In modern times lead is used as a weight for balancing tires in tire rims. No cases of lead poisoning have been related to the use of lead although it has been noted that lead from the tire weights can be lost from the tire and ground to dust along roadways. Lead loading from this source in Albuquerque was estimated to be 3,730 kg per year (Root, 2000).



Figure 3.26. Martha Washington’s wedding. Image source: <http://www.mountvernon.org/martha/marriage.asp>

Lead in Plumbing

Pure lead found a variety of uses other than sculpture and warfare. One of the most common uses for pure lead metal was in roofing and plumbing (its chemical name: plumbous). Lead was used extensively for plumbing in Roman times (Figure 3.27). It exists throughout all American housing stock that predates the 1980s. Lead pipe was used because of durability, malleability, and resistance to rust and cracking. Just as important, the interior can be smoothed to avoid turbulent flow, allowing a self filtering process as larger material settles to the bottom of the pipe.

The material is amenable to early technology. The Romans produced lead sheets by pouring molten lead into a shallow, flat bed made of sand or a mixture of dried clay and sand (Smith, 1986). The pipes were formed by wrapping the lead sheet around a cylindrical core of correct diameter, and sealing the edges together with hot lead. Figure 3.28 shows a set of 1900s plumbing tools used in the joining of pipes and in the smoothing of those pipes.

Once made, the pipes were protected from rusting. Lead rusts less than iron, but more than copper. Table D.8 shows some half reaction potentials; the more negative the potential shown, the more rustable the metal. Despite the low rustability of lead, small amounts can be mobilized from the pipes (Services, 1990). A complete miniature electrochemical cell can occur in which the lead metal conducts electrons from pit (corrosion or oxidation sites) to reductive sites (Figure 3.29) releasing soluble lead ions. Some of the lead in modern pipes derives from the use of lead/tin solder joints. (Lead has been used for 3000 years to make malleable metal alloys: see next section.) The lead arriving at the faucet can be solubilized directly from the lead pipe, or from the solder joints.

Municipal water plants can help control the lead content of pipes by the addition of polyphosphates (Figures 3.30) to create an insoluble lead precipitate coating on the pipes. (See Chemistry Example 3.1, for a calculation illustrating the use of orthophosphate solubility reactions). Other possible precipitates such as lead oxides or lead carbonate form layers too porous to thwart the rusting reaction. (In Chapter 7 we will make use of the porosity of lead oxides to design an efficient battery.) Wilmette, Illinois, is using a zinc orthophosphate for precipitation of lead which has been successful in dropping the lead content of water arriving at the tap



Figure 3.27. Roman plumbing on side of private house, Pompeii (Figure 33 in *Medicine An Illustrated History*, A.S. Lyons and R. J. Petrucelli, 1978, Abrams.

(Figure 3.30). Unfortunately, however, some of the additives fall under proprietary control and are therefore costly.

Ten years after orthophosphate additions to the Chicago water supply began a new problem arose. The City of Chicago which borders Lake Michigan supplies water to inland suburbs. The County of DuPage, where many suburbs lie, reported that the capacity of the water mains dropped. The alleged culprit is the rough surface of the phosphate layer which causes turbulent water flow and eddies. DuPage Co. attributed \$105,000 of its Water Commission's \$1.6 million electrical bill to pumping costs associated with turbulent water flow. They also asserted that the



Figure 3.28: Set of plumbing tools used in smoothing the interior of the pipe to create resistant free flow of water. (Author's collection).

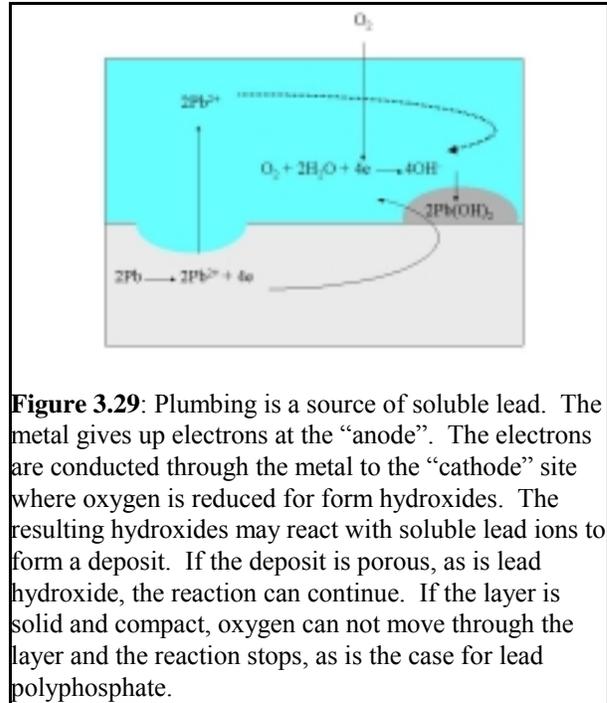


Figure 3.29: Plumbing is a source of soluble lead. The metal gives up electrons at the “anode”. The electrons are conducted through the metal to the “cathode” site where oxygen is reduced for form hydroxides. The resulting hydroxides may react with soluble lead ions to form a deposit. If the deposit is porous, as is lead hydroxide, the reaction can continue. If the layer is solid and compact, oxygen can not move through the layer and the reaction stops, as is the case for lead polyphosphate.

aluminum phosphate deposit was 1/16 an inch thick causing 8 year old pipes to operate at a 40 year old pipe capacity (Figure 3.31) (2000).

The City of Chicago was the last U.S. city to ban the use of lead plumbing in homes. The battle over lead pipes took on some unusual overtones because of the close association of labor with “The Machine” patronage system in Chicago. City Hall had been under tight control of “The Boss” Mayor Daley through the 1960s and early 1970s. After the death of “The Boss” there was a quick succession of short term mayors, followed by the election of the first African-American into the office as a reform mayor. His tenure was bitterly opposed by city aldermen in highly publicized battles known as “Council Wars”.

Use of plastic pipes was opposed by unions because plastic pipes could be fitted by nearly any person and did not require the technical skill that lead pipe plumbing did. Furthermore, labor costs could be cut by half as two person crews were no longer necessary to manipulate the heavy lead pipes. The first bill to allow plastic pipes in homes was proposed in 1983 by Mayor Jane Byrne. Alderman Ed Vrydolyak, head of the Building and Zoning Committee removed the use of plastic from the bill.

When Mayor Harold Washington, an African American, was elected mayor, some white democrats defected to the Republican Party. One crossover

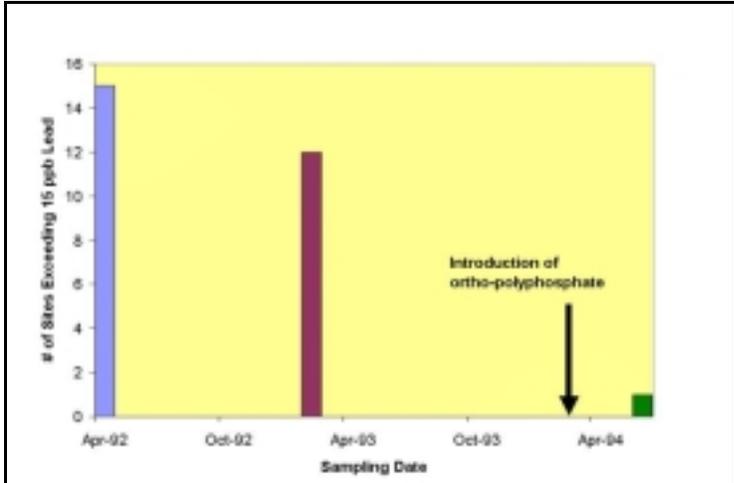


Figure 3.30: The amount of soluble lead in drinking water from the Village of Wilmette, Illinois. Levels dropped after the introduction of orthophosphate ions into the water at the processing plant.

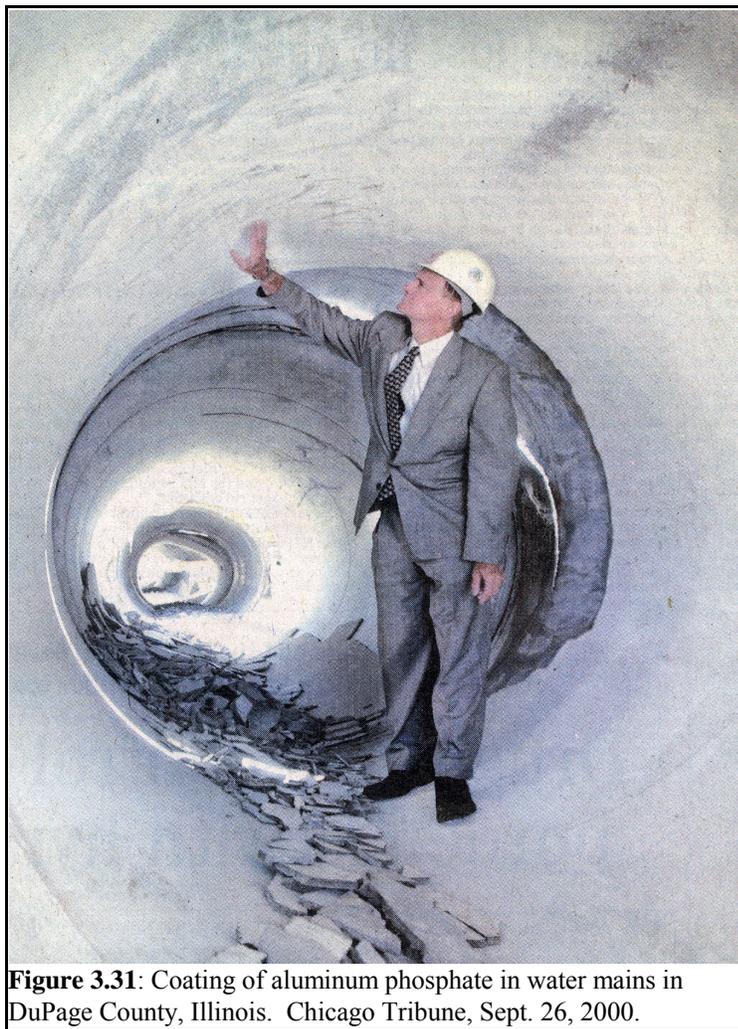


Figure 3.31: Coating of aluminum phosphate in water mains in DuPage County, Illinois. Chicago Tribune, Sept. 26, 2000.

politician was Police Superintendent James O’Grady who ran as a Republican for Cook County Sheriff. He was supported by Edward Brabec, president of the Chicago Federation of Labor. In retaliation for this defection, Alderman Ed. Vrdolyak reintroduced a bill calling for plastic pipes in 1985. When Brabec backed off Vrdolyak made no further effort to push the legislation in 1985. Julius Ballanco of the Building Officials and Code Administrators International said

They (plumbers union) are involved in the (political) machine activity heavily.

He was of the opinion that the passage of an ordinance allowing plastic was a “political crash”.

Labor cast their opposition to plastic pipe on environmental grounds. First they refused to acknowledge any hazard from lead. Local 130 of Chicago Journeyman Plumbers Unions business manager Jim McCarthy said:

I’m hard-pressed to understand why people are talking about lead poisoning. We’ve had lead pipe in the water system here for 100 years.

Second labor brought up the fact that polyvinyl chloride piping could release a number of toxic fumes were buildings to catch on fire.

Because of labor opposition and labor political strength in Chicago plastic piping did not become legal until May 17, 1990 under the second Mayor Richard Daley, Jr. [Nathan, 1985 #481], (Strong, 1986; Worthington, 1986), (Bukro, 1986; Davis and Kass, 1990).

Birth, Life, and Death Under Metallic Lead

In the early Dark Ages, a person's birth, wedding, and death could be celebrated or observed with the help of lead, all because of its anti-corrosive properties.

Lead baptismal fonts were most widely used in England, the principle lead-producing country. Lead fonts in England predate those found in France. However, it is possible that the English lead fonts simply represented a convenient way to imitate European copper fonts. Approximately thirty English lead fonts survived the destruction of the Reformation (16th century). The earliest surviving lead font in England is from St. Peter's Church, Surrey. It was originally block-pressed for embellishment into three fragments to make 12 arcades depicting battles of angels with devils (Zarneck, 1957). Some of the fonts required soldering because the sheets were cast and bent and the edges welded with the bottom added last. Other were cast whole in clay molds (Davies, 1962, plate 23). Figure 3.32 shows, not a baptismal font, but another sort of lead-based water container, an embellished horse cistern.

Worshippers were sheltered by lead. Lead has

appeared almost continuously in architectural applications since it was first used for this purpose. Lead became a practical necessity during the Norman period (1066-1150 A.D.) when cathedrals became so large. When the cathedrals became large, the associated towers could not become proportionally larger because of the weight of the stone. The English preferred to build slender spires of wood, which were covered with lead as a protection against the elements (Clifton-Taylor, 1967, p. 25). The cathedral at Ely (Figure 3.33), belonging to the Late Norman period, was modified in 1322 A.D. with an octagon tower. This tower was flanked by four tall octagonal turrets, which in turn were covered with leaded wooden spires. The total tower weight is 200 tons of timber, glass, and lead. This modified tower, belonging to the Late Decorated period replaces the original form of central tower (1100 A.D.).

Lead could be used satisfactorily on steep spires, because it could be molded out into sheets. The line of the sheets was employed architecturally to create upward -movement at a cross pattern with the stone below (Clifton-Taylor, 1974, p. 82). This technique can be seen in the Cathedral at Southwell. The principal use of lead roof, however, for the



Figure 3.32 Cistern holding water for horses. Tower of London (Photo by Author).



Figure 3.33: Cathedral of Ely, Cambridgeshire, England. Photo by A.F. The main part of the roof has metal sheets, while the tower on the right is wood sheathed with lead. (Photo by author.)

often no longer required and were regarded as an unnecessary extravagance. Lead, although expensive, was a godsend to these builders. From below these late-Gothic lead roofs are usually invisible, a fact of considerable aesthetic importance.”(Clifton-Taylor, 1967).

The use of lead in roof sheathing carried along with it certain dangers. The Cathedral of Canterbury was destroyed on September 5th, 1174 because its lead roof. A fire had broke out by the church gate and a south wind carried sparks and ashes to the roof where they became wedged between the lead covering and the decaying wooden joists. The sheets of lead began to melt, causing the entire building to suddenly burst into flame (Clifton-Taylor, 1967, p. 67).

Lead was also used for its visual effect. Wet lead reflects the sky. Weathering gives it a dark grayish tone. Occasionally it will oxidize to cerruse, or lead carbonate, giving a silver hue to the roof surface. Lead roofing was deliberately chosen by Islamic architects because the interesting contrast that its greyness lead makes with the white mosque walls. Ottoman troops under Mehmed II (1444-81 A.D.) captured Constantinople (Istanbul) on May 29, 1453. Mehmed was followed by son Selim I and grandson Süleyman (r. 1520-66), whose court architect was



Figure 3.34: Süleymaniye complex and mosque at Istanbul. Architect Sinan (1550-1557).

Sinan. The Süleymaniye complex and Mosque at Istanbul were built by Sinan (1550-1557) (Figure 3.34).

“The exterior composition of gray, lead-covered domes and white stone walls is carefully orchestrated,

medieval builder was that one could create a very good water seal on a nearly flat roof. *“In the Perpendicular period, when churches were liable to rise a good deal higher, roofs of steep pitch were*



Figure 3.35: Flashing at the base of dormer window on a house in Cambridge, England. (Photo by author.)

lightened only by the arched openings of windows and arcades arranged in threes and fives. The mosque is a logical refinement of Sinan's earlier spatial experiments and exemplifies the classical Ottoman style, in which traditional forms are repeatedly honed to perfection" (Blair and Bloom, 1994, Figure 280).

Lead can be used as a flashing or molding at roof joints to prevent the entrance of moisture. Such flashing can affect the growth of algae on roof lines, as seen on this house in Cambridge, England (Figure 3.35). Note in this figure the new and old flashing and the corresponding growth pattern of moss. Where the flashing is new there is less growth.

Lead was a much desired architectural material. Builders went to great lengths to obtain it. In 1222 A.D., the Mayor of Winchester traveled to Boston fair in Lincolnshire to buy lead for roofing Winchester castle (Cordero and Tarring, 1960). Many of the early lead-roofed buildings were destroyed during the Reformation (1500-1600 A.D.)

*You have hold to ravish your own daughters and
To melt the city leads upon your plates
To see your wives dishonour'd to your noses*

Shakespeare *Coriolanus*

Worshippers in medieval Europe could also meditate on God by viewing stained glass windows, whose colors came from lead (see Chapter 5) and whose glass pieces were held together by metallic lead "comes" (Figure 3.36). Figure 3.37 shows an early lithograph of lead came manufacturing. Figure 3.38 shows a contemporary worker (2002) repairing lead came in a complex leaded glass window.

In leaded glass work, a framework of grooved lead wire holds the glass in place. When these lead wires are cut and polished, a fine dust is generated. When they are soldered, a leaded gas phase occurs. Figure 3.34 shows a piece of English stained glass *Cistern Grisaille* dating back to 1240 A.D. It contains the original lead came and illustrates work in which the came itself forms all the design elements. Figure 3.35 depicts St. Catherine with the wheel of torture on which she died. This piece of glass, ca. 1310-1350, is from South Andrew, Woodwalton, Cambridgeshire.

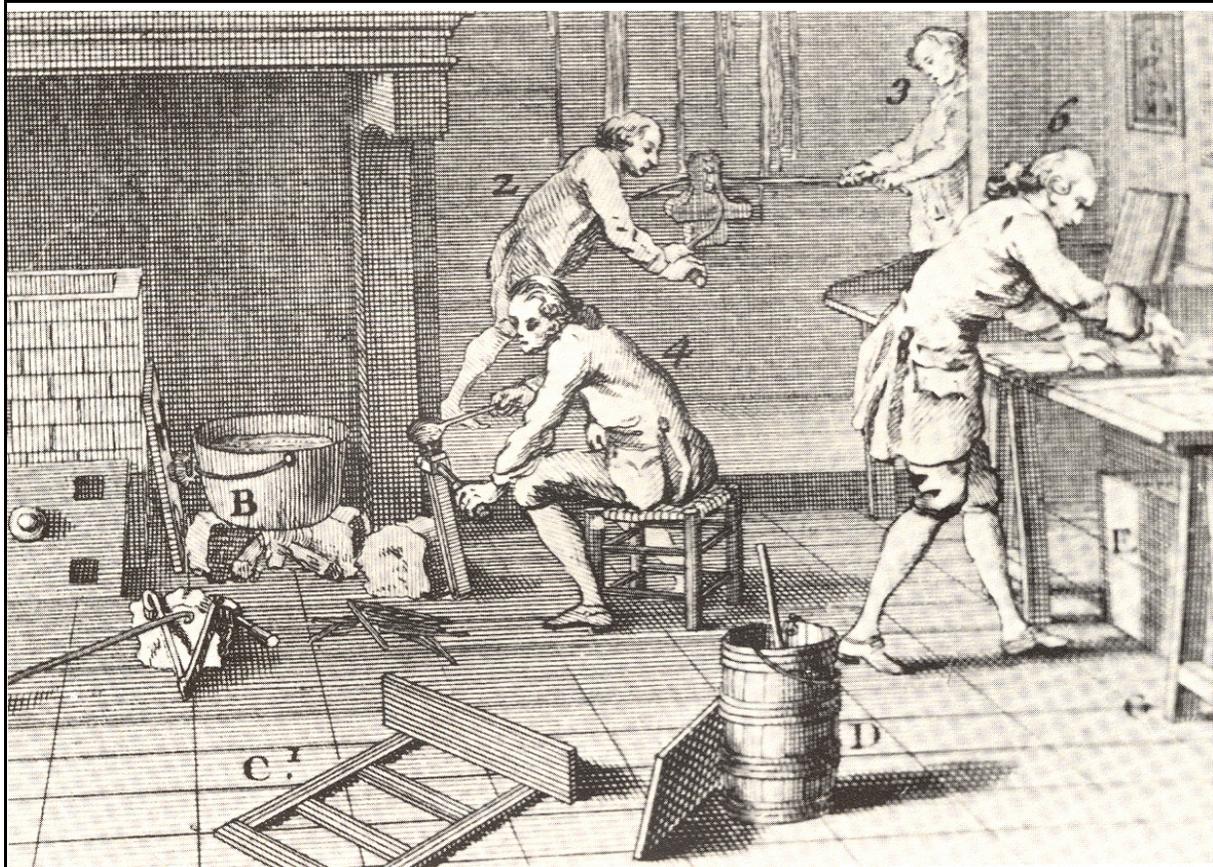


Figure 3.36. Illustration of the manufacture and recycling of lead came for leaded glasswork. Original source, Le Viel, 1774. Illustration in Alastair Duncan: *Leaded Glass, a handbook of techniques*, 1975, Watson-Guptill, N.Y.

In late nineteenth and early twentieth century American homes, leaded art glass, such as that created by Tiffany and Frank Lloyd Wright, was very popular. Leaded

glass artisans remain active in the US today. Tiffany glass workers still use copper wires soldered with lead. These contemporary artisans are thus at risk for lead exposure. According to recent studies, the respiratory intake of lead by glass workers falls under government standards. However, they tend to be uninformed about basic strategies to protect themselves from lead exposure (Pant et al., 1994), (Baxter et al., 1985; Landrigan et al., 1980). One may assume that early glass workers were routinely exposed to high amounts of lead without safeguards.

Lead came may be pure lead or alloyed with antimony or other metals to tune the flexibility and strength of the window. Lead came are desirable because they allow the window to flex under high

winds.

In England, by the Tudor period (1485-1603 A.D.), lead downspouts replaced the gargoyles used to throw water away from the edge of the roof (Clifton-Taylor, 1974, p. 121). Much of the downspout lead came from the destruction of the cathedrals and monasteries. The newly enriched reformers took it for their manor homes. Use of lead downspouts allowed for stamped embellishments and color contrast, features that can be seen at Warwick Castle (Figure 3.26).

To complete the life cycle, a person could be buried in lead. Because it does not rust, lead found use as a coffin material. Figure 3.37 shows a Sarcophagus, Tyre 2-3rd century A.D. “*Careless positioning of the identical decorative vases is typical of a mass manufacturing of articles. By having a series of standard patterns which could be interchanged and repeated, the makers were able to provide a variety of objects*” (Krysko, 1979, plate 110).



Figure 3.37. Restoration of a particularly complex piece of leaded glass uses a large quantity of lead comes. Botti Art Studios, Evanston, Illinois, Fall 2002. Photo: author.

*What say'st thou, man, before dead Henry's
corpse?
Speak softly, or the loss of those great towns
Will make him burst his lead and rise from the
dead.*

Shakespeare I King Henry VI

Metallic lead continues to be used for a

variety of purposes. Some sculptural and roofing uses have persisted although lead has often been melted down for projectiles during war. Lead pipes are still made because they rust very little. Lead roofs continue to be built because of the fluidity of the metal creates a smooth surface, thus reducing turbulent water flow.

Candle Wicks

Metallic candle wicks have historically been used in soft wax candles where the wax is burned deep



Figure 3.38. Leaded stained glass depicting St. Catherine (1310-1350) from St. Andrew, Woodwalton, Cambridgeshire, England. Currently in Ely, England. (Author).

into puddles requiring a wick that remains upright. Lead based candle wicks were voluntarily eliminated in 1974 following pressure from the advocacy group Public Citizen. In 2001 the consumer Product Safety group found that 3% of purchased candles contained lead candle wicks (Skrzycki, 2001). In response

the U.S. Consumer Product Safety Commission proposed a ban enforceable by the U.S. Customs Service on lead candle wicks. A ban effective Oct. 2003 was announced April 8, 2003.



Figure 3.39 A portion of the “Cistern Grisaille”, 1240 A.D., Ely, England. The glass is held in place with lead strips. (Photo by Author)



Figure 3.40: Down spout at Warwick castle. (Photo by Al B. Benson, III)



Figure 3.41 Lead sacrophagus with stamped embellishments dating to 3rd century A.D., Montreal Museum of Fine Arts, Horsely and Anne Townsend Bequest, (Photo by Krysko.).

LEADED BRONZES

In this section, we see how three different civilizations in three different times came to produce an alloy of bronze with high lead content. The bronzes were ceremonial.

An alloy is a mixture of two or more metals. Alloys with highly varying properties can be created through careful control of the temperature at which the second metal is added, the quantity of the metal, and the cooling. Table F.1 gives the composition of a variety of common alloys. One of the most familiar modern alloys is stainless steel, a combination of iron and carbon. The first alloys to be manufactured were bronzes consisting of primarily copper with small admixtures of (usually) tin (Sn). Surprisingly, some of the early bronzes could contain up to 50% lead.

Development of metallurgy was coupled to the taming of fire for pottery manufacture and to the use of metals in warfare. Both of these technologies required an environment that could sustain a large human population in proximity to ore bodies

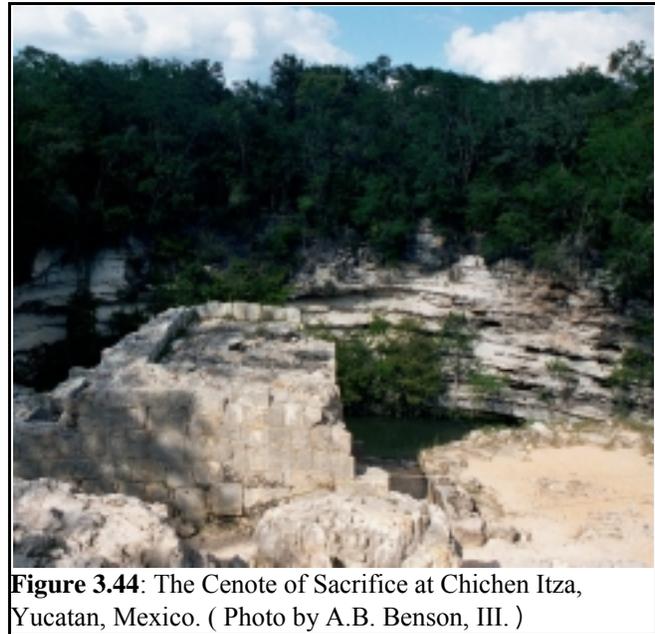


Figure 3.44: The Cenote of Sacrifice at Chichen Itza, Yucatan, Mexico. (Photo by A.B. Benson, III.)

(Diamond, 1997). Consequently the development of metallurgy took very different forms in different parts of the world.

South and Middle American Bronzes

Table J.3 gives a time line of metallurgy related history in New World. Bronzes in South America developed specific compositions based on available ores. Northern Peru and southern Ecuador alloys tended to be based on copper/silver where those ores were found. Where cassiterite (tin) rich ores were found (southern Andes, Bolivia, northern Argentina) copper/tin alloys were developed. Metallurgy in Colombia, however, exclusively used gold and copper-gold alloys cast by the lost-wax method.

These Colombian methods (Au, and Cu-Sn or Cu-Ag) were carried north to México by boat trade along the Pacific about 650 A.D. (Meigham, 1969). Merchants carried alloys north along the Pacific in return for trade of spondylium (a conch considered sacred).

Figure 3.38 shows the route of technical transmission. It is important to note that transmission was along a north/south axis, making contact harder than the east/west axis between Europe, Middle East and China. Mexico's central valley and the eastern coast of South America had similar climates but were divided by large mountains and impassable jungles, which not only prevented

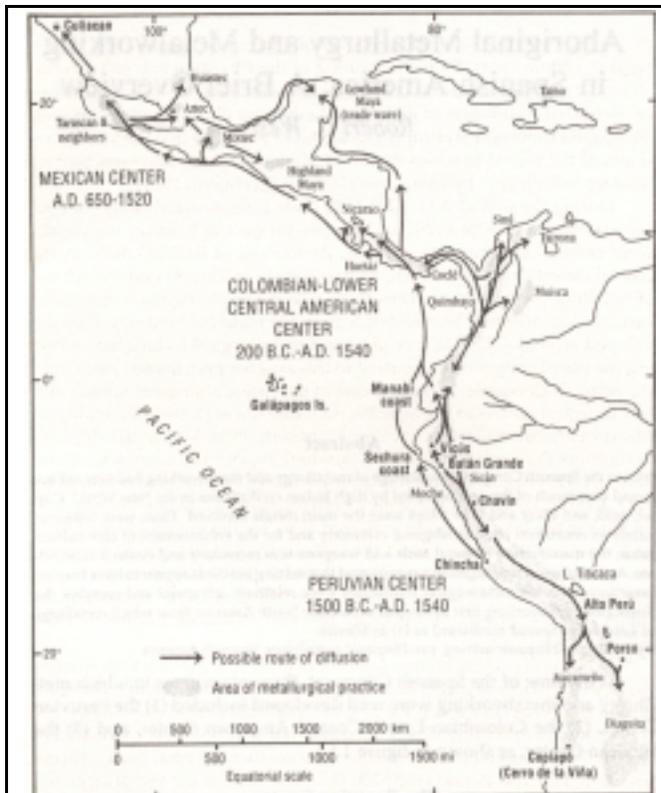


Figure 3.42: Speculative move of technology from South to North America. (Robert C. West in *Aboriginal Metallurgy and Metalworking in Spanish America. A Brief Overview in Mines of Silver and Gold in the Americas*. Ed. Peter Bakewell, Variorum, 1997, 441-73.

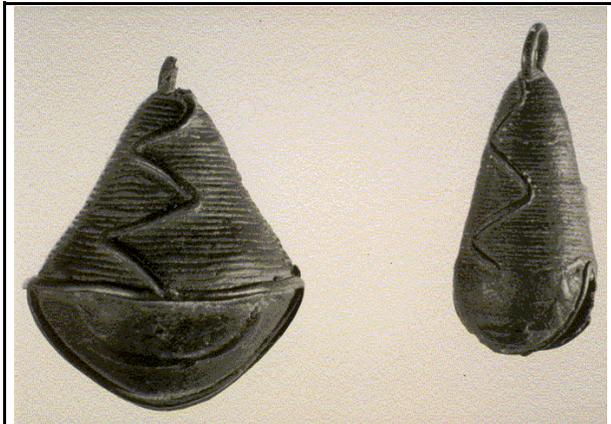


Figure 3.43: Wirework bells recovered from the Cenote of Sacrifice, Chitzen Itza, 4% lead. . ~1 inch in height. (Peabody Museum)



Figure 3.45: Chinese figure containing about 20% lead.. Kuei 40% Pb. From Chou Dynasty, 11th century B.C., Wesser Stockhom.



Figure 3.46: Example of a Igbo-Ukwa bronze which often contained up to 20% lead, Nigeria, 800 A.D. (Shaw, 1977).

motion of people, but transmission of agricultural practices.

Despite this, two different areas received the knowledge from the south: western Mexico and the region lying to the east on the other side of the Sierra Madres, where the Huastec (tributaries to the Aztecs by 1450 A. D.) were located. Their metal working was primarily based on Cu/Ag and dates from 1200-1521 A.D. Western Mexico metallurgy was based on Cu/Sn, Cu/Ag/Sn alloys, as well as some Cu/Pb alloys. It diffused to the east judging from the archaeological description of worked metal types (Pendergast, 1962). Despite the large amounts of lead-rich ores in Mexico, little lead was used, perhaps because the process of cupellation had not yet been developed. In addition, the population density had not necessitated the development of a large bronze-based warfare technology that would drive experimentation with alloy composition. This is despite the fact that metallurgy of lead was known as evidenced by the manufacture of highly pure lead objects such as a pre-Colombian lead lip plug and by the historical accounts of the Spaniards listing lead objects [Caley, 1964 #1980].

Figure 3.43 shows a “wirework” bell found in the Mayan Cenote of Sacrifice (Figure 3.44). It has been determined to be made of cast copper with greater than 4% lead (Coggins and Shane, ; Lothrop, 1952). This object looks like a wire that has been wrapped and soldered, but is in fact cast as a single unit. Wax threads were wound around a core of desired shape until the body was complete. Over this thread was placed additional mold. Then the metal was poured into the wax. The name “lost-wax” is given because the wax was lost during the casting procedure. These bells were found in quantity in the Valley of Mexico and in the State of Michoacan, and were traded to Florida and Arizona. The technology apparently derived from the manufacture of similar wire-like bells in South America. South American bells used a combination of copper and lead, whereas the

Mexican ones were made of a copper-tin alloy [Hosler, 1992 #1981].

The minimal use of lead in the pre-Colombian New World is of importance in environmental studies. The bone record of these cultures gives an approximation of “natural” lead exposure.

North America

In the land lying between the Appalachians and the Mississippi River, North America had an agricultural population based on corn production as well as abundant copper ore deposits. In this region, hammered metal work of copper took place. Tempering of the metal during cold and hot working is a means of facilitating phase changes to obtain a desired mix of structures in the final cooled material. Phase transitions in Cu/Sn alloys can be accomplished by varying the temperature but holding the material constant. The use of cold and hot tempering can be deduced from stress lines observed in scanning electron micrographs, SEM (Braidwood et al., 1951). The copper of the Great Lakes region was never subjected to temperatures high enough to achieve either the melting of gold or copper (1060 °C to 1080 °C) (Wertime and Wertime, 1982, p. 23).

Africa

Agricultural development was difficult on the African continent. The large number of diseases and

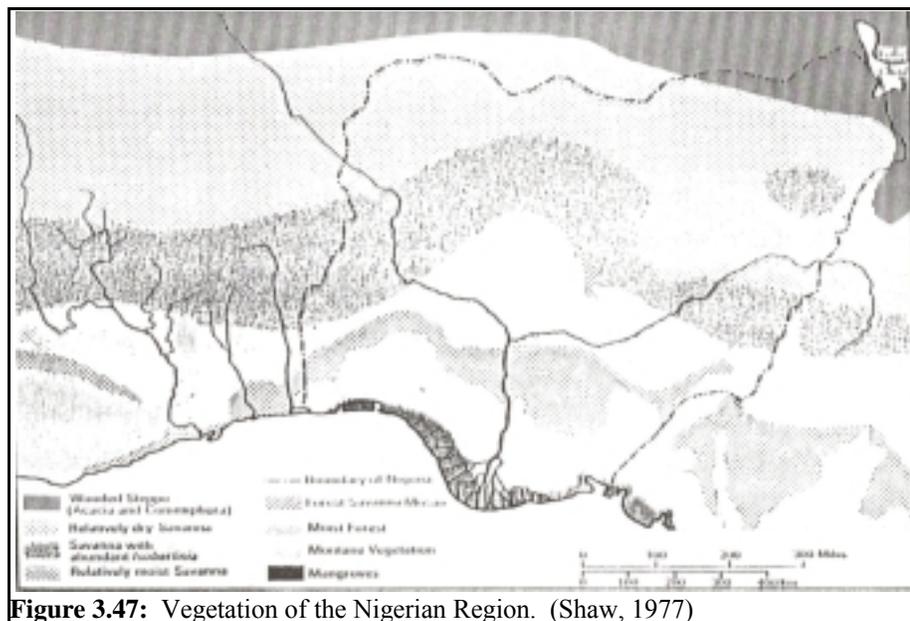


Figure 3.47: Vegetation of the Nigerian Region. (Shaw, 1977)

fungi made food storage difficult in the more tropical regions. While food storage was not a problem for hunter-gatherer cultures, it posed a problem for urbanization and division of labor, which require food transport. Cultural transmission of technology was impeded by vast deserts lying to the north and jungles to the south. Despite these problems, the Sahel of Africa had domesticated sorghum, African rice, and guinea fowl by about 5000 B.C. and tropical West African yam and oil palm (but no animals) by about 3000 B.C.

The vegetation of the Nigerian area is oil palm bush (Shaw, 1977) (Figure 3.47). The original natural vegetation was difficult to farm tropical rain forest, but 20,000 years ago it changed to a drier savannah. By 5000 B.C. tropical rain forests had returned to the area, and hunting and gathering had become the predominate economic activities. Yams were grown in the dense forest, and oil palms were grown. When food resources in the southern part of the savanna became inadequate to support population, groups moved into the forest, resulting in a sizable settlement of southern Nigeria some 2,000 years ago. The earliest known settlement which has left remains that survived the climate is that of the Nok dated to 800 B.C. to about 200 A.D. (Time line J.4)(Willett, 1971).

There are apparently three main periods of metalwork in this area of Africa. . These four settled areas -Nok, Igbo-Ukwu, Ife, and Benin - all lie within 200 miles of each other.

The bronzes of Benin are the best known, as they have been under continuous production since the 1400s. Benin was urbanized enough to establish diplomatic ties with Portugal in the mid-1400s (Time line J.4). The bronzes of Benin have historically contained lead. The lead source was originally thought not to derive from Africa as research in the first half of the 20th century could not locate a local ore with an lead isotope match [Goucher, 1978 #400, p. 278]. In addition, the lost wax production methods were similar to those used in making Ife bronzes. Finally, the composition of the Benin bronzes is similar to that of East African zinc rich brasses. These facts led to the hypothesis that Benin copperwork was originally imported from both East Africa (a region influenced by trade with Indian and having its own zinc metalwork) and from Europe.

The Ife bronzework tradition preceding that of Benin has also been closely studied. Glasswork contemporaneous with the Ife bronzes apparently was traded from Italy. This finding suggests that the movement of the Arabs in the 8th century not only included motion around the Mediterranean of North

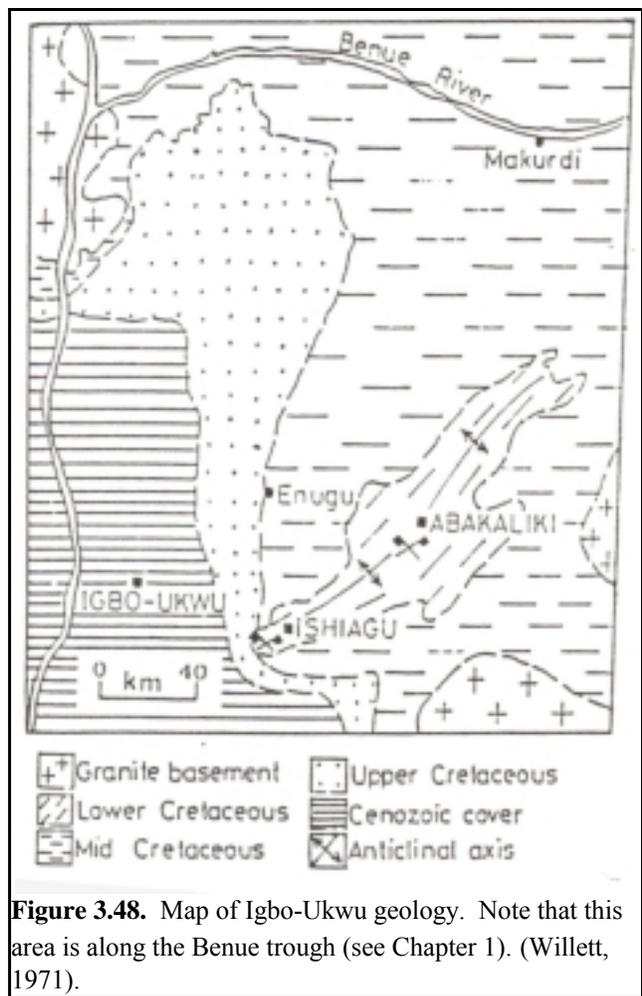


Figure 3.48. Map of Igbo-Ukwu geology. Note that this area is along the Benue trough (see Chapter 1). (Willett, 1971).

Africa but across the Sahara as well. Glass beads from Ife sites are mostly potassium-based glasses (a European type of manufacture). Monochrome beads were apparently traded from India or the East African coast. These date to 700-1500 A.D. Polychrome beads may be from Venice, since glass bead work started in Venice during the 5th century A.D. (see next Chapter 4) and developed into a fine art by the 12th century A.D. Export of beads from Venice began sometime during the Crusades of the 10th century A.D. (Shaw, 1977, p. 82).

The cultural transmission argument is thus bolstered by the known trading routes. Arab conquest of North Africa in the 600s disrupted trading patterns from Nigeria to Rome and Carthage. Arabs regained trade routes to gold-bearing West Africa. These trade routes started from Egyptian oases and headed south and east through Wanyanga and then west towards the middle Niger bend. Ancient Nigeria trade routes were probably not based on gold but on African elephant

ivory which ended up as far away as 12th century China. African ivory was preferred over Indian ivory because the tusks were larger and easier to carve, and had a more attractive grain.

More recent excavations (ca. 1956 A. D.) from an earlier dated site, Igbo-Ukwu, unearthed bronzes which were originally assumed to be based on imported copper sources (Shaw, 1970). However, the Igbo-Ukwu bronzes are stylistically very different from Ife. They can also be dated as earlier than or contemporaneous with Ife works. The bronzes of Igbo-Ukwu were high in lead and made by a technique that had not been practiced in the Mediterranean for over 900 years. In this technique, a precursor to the lost wax method, a bowl-like mold is made and a second clay part held with wedges inside the first to create the hollow interior of the final object.

The source of the metals used at Igbo-Ukwu differs from that used at Ife (Willett, 1971, p. 31) (Craddock et al., 1997) (Figure 3.48). Isotope analysis of these bronzes show them to be unrelated to those of Benin. Their source areas were North and Central Africa. An anciently worked copper ore body was then discovered less than 100 km away from Igbo-Ukwu. Its isotope ratio matches that of the bronzes. A later account of the site suggests that independent metalwork developed through the discovery of ore bodies along the Niger River (Chikwendu et al., 1989; Fleming and Nicklin, 1982).

Like the Chinese, the Nigerians discovered that a very high lead content would allow fluidity in the bronze casting. Igbo-Ukwu bronzes are high in relief and detail. Figure 3.46 shows an object of lead and bronze from Igbo-Ukwu (Shaw, 1977, Figure 3-24). A similar hippopotamus sculpture contains 31.6% lead.

Another metalworking area of Africa was central Zambia in the 5th century A.D. (Fagan, 1971). Settlement in this area was constrained by sleeping sickness, a disease transmitted by the tsetse fly.

Middle Eastern Bronzes

At one time the Middle East (Mesopotamia) was credited with all metallurgical developments that occurred on the Eurasian and African continents. More recently it has been thought that metallurgy arose independently in various areas.

The composition of some Mediterranean and Middle East bronzes is shown in Table E.3 (1). The tin content is relatively stable, at about 10% while the lead content fluctuates greatly. The small amount of lead

in bronze often resulted from impurities in the tin.

In general, the Mediterraneans, Egyptians, Mesopotamians, Greeks, and Romans did not employ much lead in bronze, until the Middle Ages when the casting bronze of choice was gunlead. One exception to this is the statue of Marcus Aurelius. Portions of this statue, which dates from 180 A.D. contains 20% lead (de la Croix and Tansey, 1970; Ferretti et al., 1989).

Chinese Bronzes

China has a long metallurgical history. For much of the 20th century, it was assumed that Chinese metallurgy was an import from Mesopotamia. This is because the earliest metallurgical remains in China are mature works without evidence prior rudimentary bronze-working (Watson, 1974, p. 37).

Most of the information about Chinese metallurgy, came from English excavations in the late 1800s and early 1900s and from analysis of bronzes in European museums. Until the 1980s, archaeological work was not a priority of the People's Republic of China because it fell outside the dictates of Marxist theory (Press, 1978). Recent Chinese archaeological work has taken place in the north. Copper knives and awls have been discovered in Shinsi, Kansu, and Shantung. These date back to 3000 B.C. and earlier and suggest that experimentation with metalwork occurred prior to the use of fullfledged metal casting (Hsu and Linduff, 1988; Yun, 1986).

Wagner discusses of the diffusionist vs anti-diffusionist argument (Wagner, 1993, p. 28-33). He dismisses the early assertions of diffusion of metalworking from the Mediterranean to China as based on a faulty archaeological record and the propensity of 19th century Europeans to have contempt for the non-Europeans. Thus Terrien de Lacouperie could write in 1894 that Chinese civilization was "a loan, a derivation, an extension eastward from a much older form of culture in the west". Wagner ascribes this view to "a psychologically necessary belief that the subject peoples of the European colonial powers were racially incapable of creativity of the same order as that of Europeans." He further faults the diffusionists with claiming inventions of a massive magnitude can arise only once and that they must follow the same path in development. The anti-diffusionists (Barnard, 1961; Barnard, 1980; Barnard, 1983; Barnard and Sato, 1975; Cheng, 1960; Ho, 1975) state that six questions are answered in favor of independent origin of

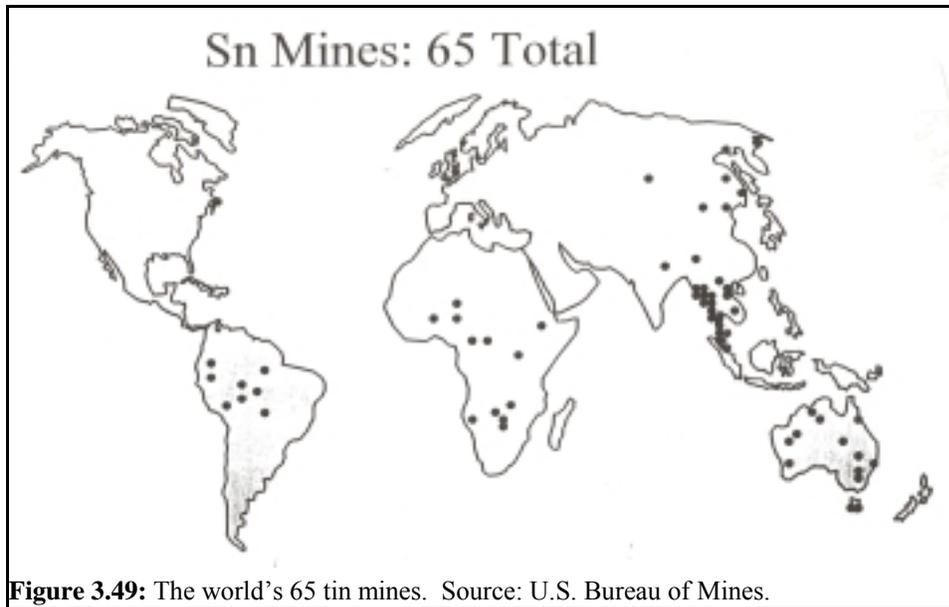


Figure 3.49: The world's 65 tin mines. Source: U.S. Bureau of Mines.

determine if A affected B, C, and D and thence E or if A directly caused E. As a result historical arguments assigning a direct cause to an event are difficult.

Chinese bronzemaking was dependent upon the relative peace and the magnitude of the Chinese empire. It required both sources of both tin and copper which were geographically spread out. Early bronzemaking depended upon the skill

metallurgy.

1) There is archaeological evidence for earlier bronze work.

2) Copper and tin deposits are readily available (Figure 3.39).

3) Some forms of Chinese objects can be related to other neolithic technologies.

4) Chinese bronze metallurgy reveals major technological differences from Mesopotamian. There appears significant amounts of zinc. (The diffusionists argue that these artifacts have been misdated as such technology was unfeasible (Muhly, 1986). Others have shown empirically that high zinc copper alloys could be obtained by low temperature smelting from mixed copper-zinc ores (Sun and Han, 1981).)

5) Geographical spread of metallurgy was centrifugal (from center out), not centripetal (from the edge in).

6) Stylistic affinity of An-yang work with Eurasian steppes is not close enough to suggest transmission of bronze working across the steppes.

Barnard concludes that the anti-diffusionist argument is logically incapable of empirical proof, but that diffusionists should be able to come up with proof. If an idea derives from one source, there should be a linguistic root referring to that source.

There is the additional fact that if there were a million simultaneously, and independently, developing cultures, it would still be difficult to assign the statistics of causality for a multiple-cause event. By this we mean that if agents A, B, C, and D act together to produce event E it would be difficult to

and knowledge of Shang dynasty (16-11 century B.C.) and Zhou dynasty (11 century to 221 B.C.) artisans (Time line J.5). With the fall of these dynasties, the technology decayed. Bronze working again arose during the period of the Mongol period (ca. 1253 A.D.), particularly after the subjugation of the metal-rich Yunnan provinces (Kerr, 1990). Compare Figure 1.11 and Figure 3.49 to see the overlap of tin and lead mines necessary for the development of bronze working.

The earliest leaded bronzes in China were not accompanied by silver impurities. Apparently their lead ore derives from cerrusite which is abundant in north China (Barnard and Sato, 1975). The amount of lead in Chinese bronzes increased over time (Motonosuka, 1953). (See Time line J.5 for Chinese chronology). Gettens suggests that 5-10% lead in Chinese bronzes in the first millenia was very common. In the Freer gallery the earliest 14 pieces (Northern Wei Dynasty (386-534 A.D.) had an average of 5.1% lead. Pieces from the Northern Qi dynasty (550-577 A.D.) had lead average of 21%. Tang dynasty (618-907 A.D.) bronze had lead content well above 20%. These changes in bronze lead content mirror the changes noted in bronze coinage in China discussed in Chapter 2.

The amount of lead in very early Chinese bronzes is so constant that it may very well be a deliberate addition. The lead content in Chinese bronzes depended upon the type of material that was cast (Bussagli, 1987). Highly ornamented and ritual

objects contained the highest amount of lead (Table E.2, Shang Dynasty). The vessels with highest lead content were thought by Linduff to be grave offerings [Linduff, 1977 #1982]. The addition of lead occurred because high amounts of lead imparted an extra fluidity to the melt, making the casting easier, bringing the molten metal into more extensive contact with the mold surface. Very fine and intricately raised surfaces could be achieved through the casting of high-lead metals.

Figure 3.46 (Chueh bronze from the Freer Art Gallery) shows a typical highly leaded bronze (containing 20% or more lead) from the Shang period [Jett, 1992 #1983]. Highly leaded bronzes were associated with highly ornamented burial objects.

Particularly ingenious use of variations in bronze properties occurs in the manufacture of swords. Swords for the King of Yue (5th century B.C., Eastern Zhou period) were made in two separate castings that were then joined together. The outer bronze was high in tin and low in lead. This composition created a brittle and hard cutting edge. The inner bronze which was high in lead, created a material capable of cushioning the shock of a blow during fighting.

Metallurgical experimentation seems to have been driven by the use of bronze in warfare. Morphological observation of a sword from the early warring state shows a grain alignment (laminar flow) that suggests tempered bronzes. This type of sword indicates great knowledge of quenching and annealing to obtain a desired composition phase of the copper tin alloy (α vs β vs $\alpha\beta$ phases) (Tangkun, 1992).

Written records confirm this level of metallurgical knowledge in which malleable metals alloyed together produce hard alloys. “Xun Zi” (300 B.C.) in *Chapter of a Powerful Nation* writes: “*Copper is soft and tin is soft too. If two soft combined, the combination will be hard.*” (Tangkun, 1992). This quote indicates that alloys of copper and tin create bronze which is harder than copper.

Analysis of bronzes from the Shang city Anyang, located near Yin Hsiu and founded by P'an-Keng about 1340 B.C, shows great variations in the composition of the metal. An object's composition depends upon its intended use. A hard alloy of zinc with small quantities of iron and antimony was used for arms and utensils. A more flexible, vibrant one with increased tin content was shaped into drums and bells. A lighter, lead-free mixture was used in arrowheads [Garner, 1960 #1984].

Metallurgy on the Indian Subcontinent

The time line for India shows an African race crossing the subcontinent about 60,000 B.C. and then mixing with later immigrants.

The first urban cultures to be formed were along the Indus River, in two major cities at Harappa and Mohenjodaro (2350-1770 B.C.), located near present-day Afghanistan and upper Pakistan (Figure 3.50). These cities had a variety of specialized craftsman, artisans, priests, rulers, and traders. Trade took place with the Mesopotamian cities of Ur, Kish, and Tell-al-Asmar). The Indus River cities were built with commodious homes and public baths (Marshall, 1931). As with Chinese archaeology, Westerners (Europeans) once thought that these cities developed through diffusion from Mesopotamia (Casal and Nindowari, 1966; Gordon et al., 1958; Heine-Geldern, 1956), although Indian scholars have demured (Chakrabarti, 1995; Lal and Thapar, 1967; Nissen, 1988; Wheelen, 1956). Again, as in China, archaeology has not been a high priority in post-colonial India.

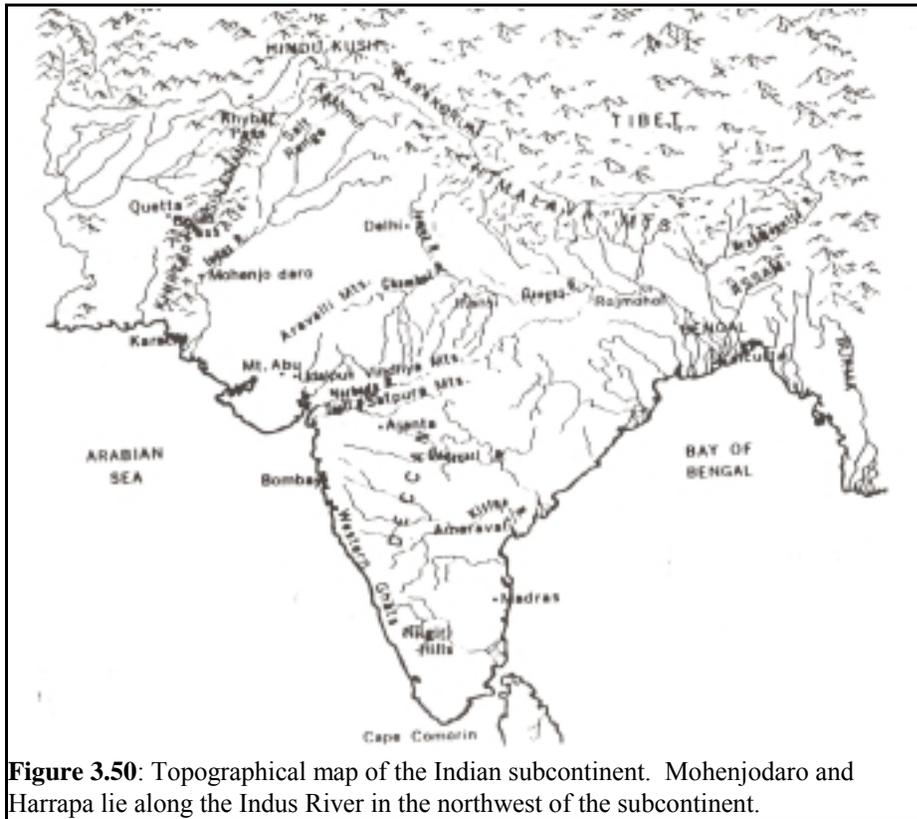


Figure 3.50: Topographical map of the Indian subcontinent. Mohenjodaro and Harrapa lie along the Indus River in the northwest of the subcontinent.

years before the beginning of the Indo-European migrations. Their end has been variously attributed to the arrival of Indo-Europeans, to climatic change that made the river-fed agriculture untenable (Bhattacharyya, 1988), or to flooding (Raikes, 1967; Shaffer, 1992; Sheshadri, 1992).

At Mohenjodaro, cotton was domesticated and, like writing, in use long before it was used in Mesopotamia. They used crude copper, refined copper, copper/tin bronzes, and arsenic/copper bronze. At Harappa, lead objects were used. Alloys of copper often contained lead.

Harrappan metallurgists smelted copper, gold, silver and lead and alloyed various ratios of these metals. A copper-lead-tin alloy has been reported with a lead content of 1 to 14.9%. Lead may have been isolated first and then added to copper for the purpose of lowering the melting temperature and increasing in fluidity (Bhardway, 1990). Of 43 materials analyzed from early Mohenjodaro, 6 contained significant amounts of lead (Table E.4, (Agrawal, 1990)). Only a small fraction of the materials found were alloyed. Out of 177 artifacts found, 70% were unalloyed, and 30% contained 1% tin. The paucity of articles with tin

may be due to a lack of tin supplies. Other alloying materials were As (8% of the objects), Ni (4% of the objects), and lead (6% of the objects, with lead content ranging from 1-32%).

The mines of Zawar in Rajasthan (see Chapter 2) have large deposits of lead which may have been used by the Harappan civilization. Isotope composition studies have not yet been performed. Pure lead was used as plumb bobs. Several lead ingots have been found at Mohenjodaro. Lead ore has also been found in the form of galena (Agrawal, 1990).

These cities abruptly died out a few hundred



Figure 3.51: Pyrolusite (MnO₂) dendrites form from the edge of a cleavage plane on sandstone. (Author's collection)



Figure 3.52 A slice from a geode. The solidification of various mineral layers occurs from the edge inward. The center of the geode shows dendritic formations as compared to the solid layers formed around the edge. (Author's collection)

Why Is Lead Added to Some Kinds of Bronze?

Lead appears in alloyed metals from three spatially and temporally disparate places: wirework bells in Mexico, the Igbo-Ukwu highly textured ornamental bronzes from Nigeria, and the intricate burial bronzes of the Shang Chinese. All three types of metalwork show high relief and ornamentation (compare Figures 3.43, 3.45 and 3.46). Why was lead used in all of these bronzes?

Lead, like most other additives to copper alloys, can solve a major problem that occurs in working with pure copper metal. Although the earliest copper metalwork was

hammered, the process is difficult because of its hardness (Ma, 1986). The Mohr scale is a measure of hardness. It places talc at 1 and diamond at 10. On this scale, an orthoclase rock has a hardness of 6 to 6.5, copper a hardness of 2.5 to 3, and lead a hardness of 1.5. While copper is more difficult than lead to hammer into useful objects, it is not as durable or hard as a stone implement. Copper knives dull easily. In addition, copper oxidizes in a way that may detract from its beauty as a ritual or art object.

To solve the difficulty of hammering copper into shape, the metal can be melted and then cast. Using a molten system introduces several new problems. These are 1) gas content; 2) fuel requirements; and 3) control of the hardening or solidification process.

The addition of lead helps to alleviate all three problems. Adding lead to the Cu/Sn bronze mix reduces the amount of gas which can be dissolved into the molten metal. Addition of lead to the bronze mix also reduces the temperatures required to liquefy the metals for casting. Finally, and most importantly, addition of lead to the bronze prevents the molten metal from prematurely solidifying and clogging the mold. As the melt solidifies, beginning at the exterior surface and moving inward, dendrites form (Figure 3.51). If such dendrites form inward from a pipe, the internal

diameter of the pipe decreases and the flow of the molten lead ceases, often before the pipe end is filled. Figure 3.52 illustrates inward solidification in a geode. The center of geode is clogged with dendrites. Similar structures can be observed in clogged metallurgical molds. Addition of high amounts of lead (15-20%) prevents dendrite formation by creating an internal lubricant. High amounts of lead are found only in ornamental bronzes, as lead tends to soften or weaken other bronzes used for agriculture or warfare.

BRASS

Bronze is an alloy that consists predominately of copper with a second major metal as tin, followed by small additions of lead (Table F.1). A similar alloy is that of brass. In the case of brass, the predominate metal may be zinc (2-80%), followed by copper (20-97%), tin (0-14%), and then by lead (0-12%). It has a more brilliant sheen to it than bronze.

A contemporary alloy that uses lead is “red brass”, a Pb-Cu alloy used primarily in plumbing or in naval applications (Table F.4). Its 4-8% lead composition makes it easy to machine. However, there is a fear that the lead smeared across the surface during machining could be leached. Replacement of lead by Bi has been proposed (Whiting and Sahoo, 1995). Bi could substitute because of its properties, economics, and toxicology. It can serve the same purpose as lead by spreading around the copper dendritic grain as it grows. Denver based ASARCO introduced a product called EnviroBrass in late 2001 which contains 0.01 to 0.25% Pb. The machining capacity of the brass is retained by use of bismuth and selenium (2001).

NIELLO

Description and Chemistry of Niello

During cupellation (the separation of silver from other metals, as described in Chapter 2), gold is not separated out. Gold oxide decomposes at a low temperature to gold metal, which is miscible with liquid silver. In addition, gold metal is of a high density and thus does not float with the liquid PbO.

How was this problem solved? When they first learned to handle silver ores, the metallurgists became familiar with lead sulfide and silver sulfide properties. They found that the metal sulfides formed alloys and eutectics. A eutectic is an alloy whose composition gives the lowest possible melting point. These metal sulfides particularly form a hard, shiny black material used to inlay bright coinage metals of

Table 3.1: Data Important for Niello

<u>Material</u>	<u>Melting Point C</u>
Pb	327.5
Cu	1083
Au	1064.4
Ag	961.9
Ag ₂ S	825
Au ₂ S	decomposes 240
Au ₃ S ₃	decomposes 197
Cu ₂ S	1100
PbS	1114
5 Ag ₂ S: 7 Cu ₂ S: 8 PbS	440

Au, Ag, and Cu. This material is called niello (Maryon, 1971). The process for separating silver from gold using lead may have been discovered during the learning curve for niello production.

Chemically speaking, what is niello? Niello from Egypt, ancient Greece, and Roman periods, as well as from early Celtic work, is apparently a pure silver sulfide (Moss, 1955). Silver sulfide is worked at elevated temperatures (825 °C) (Table 3.1). The temperature control must have been exquisite because the metal object that was being inlaid melted (Ag = 961 °C) only 50-100 °C higher than the silver sulfide (Ag₂S = 825 °C) worked into the silver. This suggests that ancient metal objects inlaid with the black sulfide material were not first subjected to high temperatures. Rather, they were cold worked (hammered) to achieve localized heating from localized pressure. We know today that increasing the pressure by hammering raises temperature (PV/nR = T). If the volume remains the same, as well as the number of moles, localized hot spots can occur where pressure is applied.

The northern Europeans in the early centuries after the fall of the Roman Empire were masters of inlaid black on metal. During that era, many mass migrations took place, and artworks had to assume mobile forms such as bracelets, helmets, swords, chalices, rings, and books (Kitzinger, 1983). Figure 3.453 shows events occurring as the Huns moved from areas north of China toward Europe in 200 A.D. The fall of the Alans in 375 A.D. provoked movement of the Alans to the west, created a domino effect that terminated with the sack of Rome by the Vandals.

The Ag₂S hammered “niello” inlay of this period culminated in the Celtic/Anglo-Saxon work in

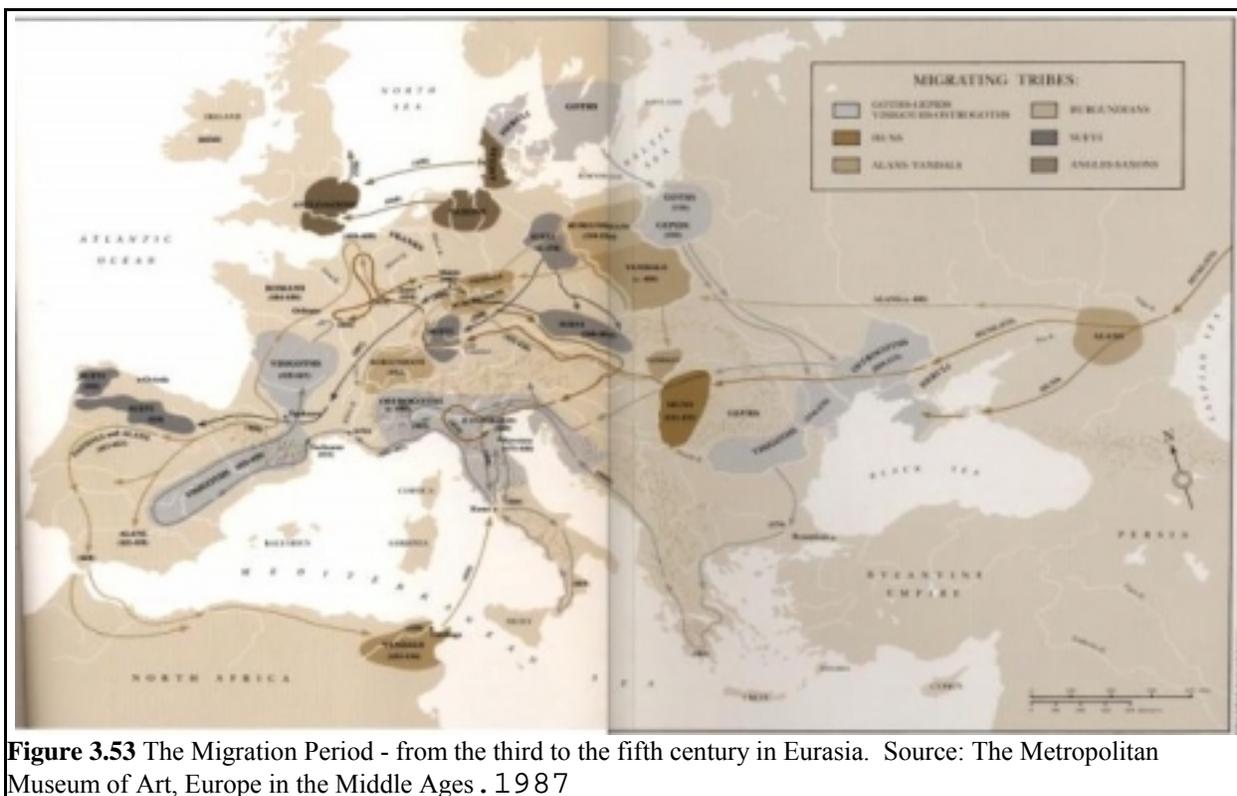


Figure 3.53 The Migration Period - from the third to the fifth century in Eurasia. Source: The Metropolitan Museum of Art, Europe in the Middle Ages . 1987



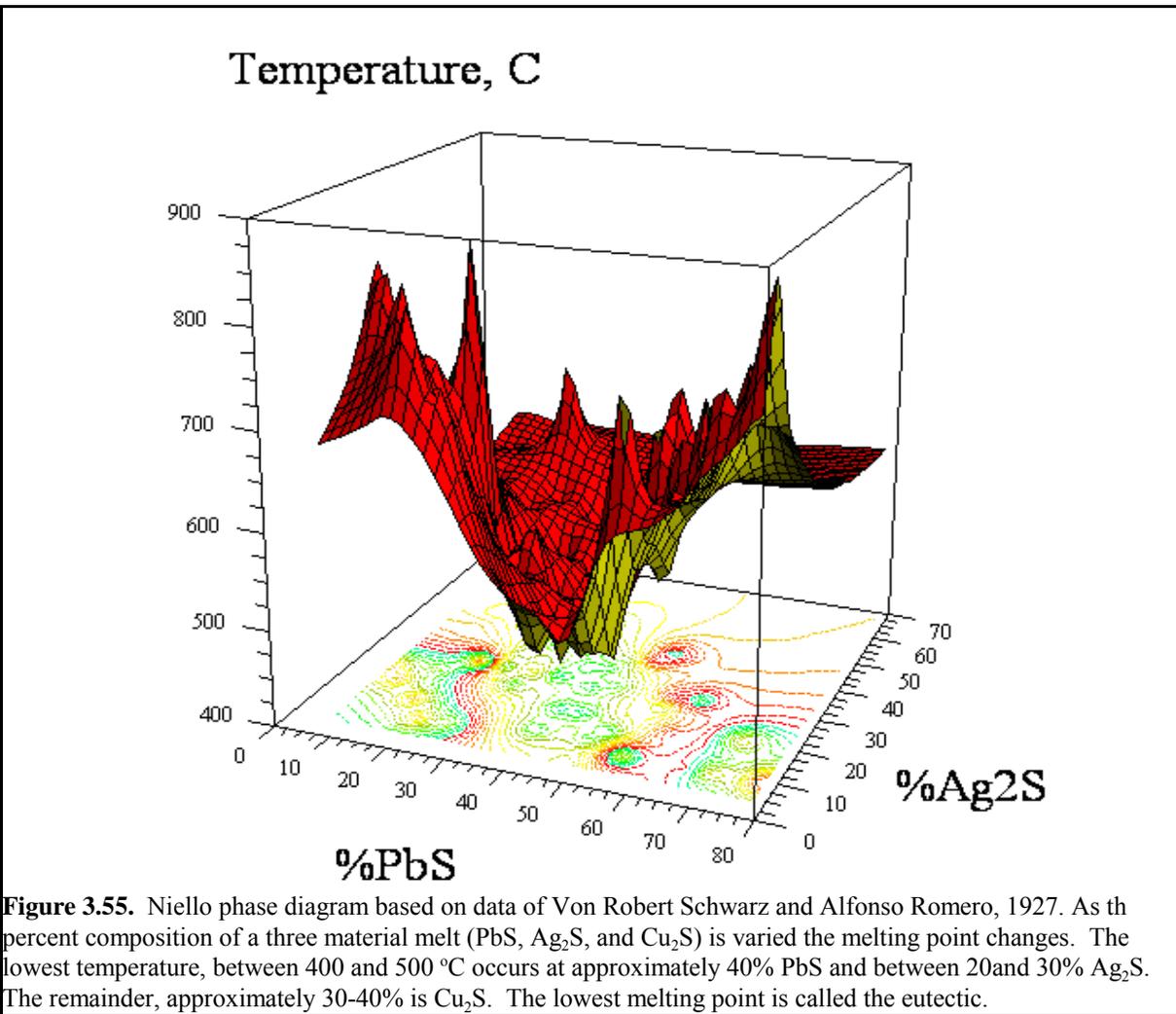
Figure 3.54: Viking brooch with niello star at right hand side and markings on the “handle”. Photo by A.F.

England. This work was epitomized by the material recovered from the Sutton Hoo Viking burial and the Fuller brooch, as well as finger rings from Alfred the Great’s court. (See Time line Appendix J.6 for a relevant time line of Dark Ages England). A niello piece from this time period is shown in Figure 3.54.

Sometime in the Middle Ages, the alloy of PbS, Ag₂S, and Cu₂S was adopted in niello work. This type of niello had the advantage of lower melting points (Table 3.1). The structural phase diagram is shown in Figure 3.55 (Schwarz and Romero, 1927).

Ag⁺ to S²⁻ has a cation-anion radius ratio >0.6 implying a cubic body centered arrangement of anions (the same structure as table salt, NaCl). As more copper is added the structure changes. Cu⁺ to S²⁻ has a ratio of <0.6 leading to a zinc-blende structure. The structure of the copper sulfide varies from high to low temperature. The low temperature form is called digenite (Cu₉S₅)(Djurle, 1958; Donnay et al., 1958). Lead sulfide has a NaCl structure (Table F.6B). The interplay between these structures gives rise to the eutectic with its low melting point. Eutectic formation depends upon the crystal phases adopted by the various components.

Remarkably, the melting point can be lowered from that of pure Ag₂S at 825 °C; Cu₂S at 1100 °C; or PbS at 1114 °C to 440 °C for the eutectic of 5: 7: 8 parts, respectively. This melting point is so low that the object to be inlaid could be subjected to heat and still melt the black inlay.



After niello is fused to metal, its surface can be polished to a reflective, permanent, uniform color. The color ranges from dark gray to deep black depending upon the alloy composition.

The *Mappae Clavicula* (900 A.D.) has a very garbled recipe for the “true” alloy of niello:

Recipe 89-B Black Inscriptions on Silver

Grind a little burnt lead in a mortar, mixing in some sulphur and with vinegar make it the consistency of glue. Inscribe silver vessels and when it has dried, heat them, and it will never be worn off.

Recipe 206: Painting Black on Gilt Vessel, so that you think it has been inlaid

Melt equal parts of red copper and lead and sprinkle native sulphur on, and when you have melted it, let it

harden; put it in a mortar, grind it, add vinegar, and make the ... with which writing is done of the consistency. Write whatever you wish on gold or silver. When it has hardened heat it and it will be inlaid. Now it may be melted like this: cut a cavity in a piece of charcoal, and put silver and copper in it; melt them, and when they become liquid mix in lead, then sulphur, and when you have mixed it pour it out and do as was said above.

Monks copied recipes such as the above from other copies. Thus this recipe has little practical value. The recipe of the metal worker Theophilus is much easier to follow. In the late Middle Ages, Theophilus described the alloy of silver /lead sulfide, which forms a low melting eutectic (see Table 3.15).



Figure 3.52: Russian Niello from the time period of Ivan the Terrible.

Book III, Chapter 28

Take pure silver and divide it into two parts of equal weight and add to it a third part of pure copper. When you have put the three parts into a small casting crucible, weigh out lead to equal half the weight of the

copper that you mixed with the silver. Take yellow sulphur and crush it small; put the lead and some of the sulphur into a small copper pot and put the rest of the sulphur into another casting crucible. When you have melted the silver with the copper, stir them both together with a piece of charcoal and immediately pour into them the lead and the sulphur from the small copper pot. Mix it all again vigorously with a piece of charcoal and hastily pour it into the other casting crucible over the sulphur which you have put therein. Quickly lay aside the crucible you have poured from and pick up the one you have poured into, and put it into the fire until [its contents] melt. Stir it again and cast it into an iron ingot mold. But before it is cold, hammer it a little, then heat it slightly and hammer it again, and so continue until it is completely thinned out. For the nature of niello is such that, if it is hammered when cold, it immediately breaks up and flies into pieces; on the other hand it should not be heated so much as to become red because it immediately melts and runs into the ashes. When the niello is thinned out, put it into a deep, thick pot, pour water over it, and crush it with a pestle until it is extremely fine. Then take it out and dry it. Put the fines in a goose quill and stop it up; put the coarser parts again into the pot and crush them and, when they are dry again, put them in another quill.

Theophilus' recipe consists of 56% Ag_2S , 30% CuS , and 14% PbS . The niello described is not the eutectic, but still has a low melting point so that the metal can be heated with the powdered niello without damaging the object. Theophilus' niello melts between $440\text{ }^\circ\text{C}$ and $560\text{ }^\circ\text{C}$. His recipe for the application of niello follows:

Chapter 29: Applying Niello

When you have filled several quills in this way, take the resin called borax and grind a small piece of it with water in the same pot, so that the water is rendered just turbid from it. Wet the place you want to cover with niello with this water first; next, take the quill and with a light iron rod shake out the ground niello carefully over the place until you have covered it all, and do the same everywhere. Then heap together well-burning coals and put the bowl into them, covering it carefully in such a way that no coal is placed over the niello or can fall on it. When the niello has become liquid, hold the bowl with tongs and turn it everywhere where you see the niello flowing, and in so turning be careful that the niello does not fall to the ground. If it does not become full everywhere at the first heating, wet it again and put niello on as before, and take good care that more is

not needed.



Figure 3.53: Detail of niello inlay on a 1865 Russian beaker. Collection of author. Photo by A.F.

Moss summarizes various historical recipes and estimates the temperature range from the phase diagram (Table F.10). Table F.11 shows some contemporary recipes for niello. In some cases antimony is used to achieve a finer black color (2 parts silver, 3 parts copper, 1 part antimony, 1 part lead, and 1 part sulfur) (Feldveg, 1975).

A modern version of the niello recipe has been printed for contemporary metal workers (Untracht, 1982, p. 282-386). It is paraphrased as follows. This recipe seems almost perfectly derived from that of Theophilus.

Carve out gold or silver and heat the niello alloy on it. Use a new clean carbon containing crucible to limit the amount of oxygen in the melt. First fuse copper with silver with boxax to promote liquefaction and control oxygen uptake. When melted stir them with a charcoal stick or graphite rod. Moderate the heat and add lead which has been mixed with sulphur. Play a reducing flame on the crucible bottom until it becomes dull red and contents are fully fused. Cool on a clean stone, and hammer thinner, break apart and grind with mortar and pestle. Place niello paste over the grooved surface of the metal with a spatula, fuse with a reducing flame (charcoal). Scrape away remainder (after fusing) with a sharp knife, grind with pumic paste, do not rush.



Figure 3.54 Russian souvenir spoon decorated with niello floral pattern. This niello would have come into contact with saliva . Niello can easily be rubbed off and can contribute to lead poisoning.

Italian artisans brought niello work to a peak. Until recently, it was



Figure 3.55: An example of Siam Sterling Silverware with the traditional dancers on two bracelet links. Note the difference between this style of Niello which uses a solid background of black as compared to that of the Russian style, which uses a solid background of silver. Author's collection.



Figure 3.55. Close up of the inlay from Figure 3.56.



Figure 3... Bukhara tribal ring. Author's collection.

also produced in Turkestan (Central Asia), the Caucasus region of Russia and Turkey.



Figure.... Central Asian traditional knife, approximately 1 foot long, hilt and sheath decorated in niello. Author's Collection.

In Russia niello is called *chern* and has been employed since Byzantine times [Goldberg, 1952 #1988]. From the time of Ivan the Terrible (1547), niello has been distinguished “*by exquisitely proportioned figures with beautiful silhouettes and by impeccable technical execution*”. An example of such work is the reliquary commissioned by Tsar Fedor Ivanovich for his wife, Irna. This reliquary derived from the Kremlin Workshops in 1589 (Museum, 2000) (Figure 3526). In the latter part of the seventeenth century flower motifs were popular in Russian niello, which was often combined with increased carving. In the nineteenth century, the technique of smooth niello engraving came into vogue. In this technique, the background around the picture is not decorated. This change in detail was driven by a need to reduce cost. There was a surge in the production of souvenir niello upon the end of the Napoleonic Wars, when many objects were decorated with sentimental locations. One such object is a small niello silver cup from the mid to late 1800s (Figure 353). Also shown is a spoon whose curved back comes into contact with the mouth. This spoon is extensively decorated with a flower motif (Figure 3.54).

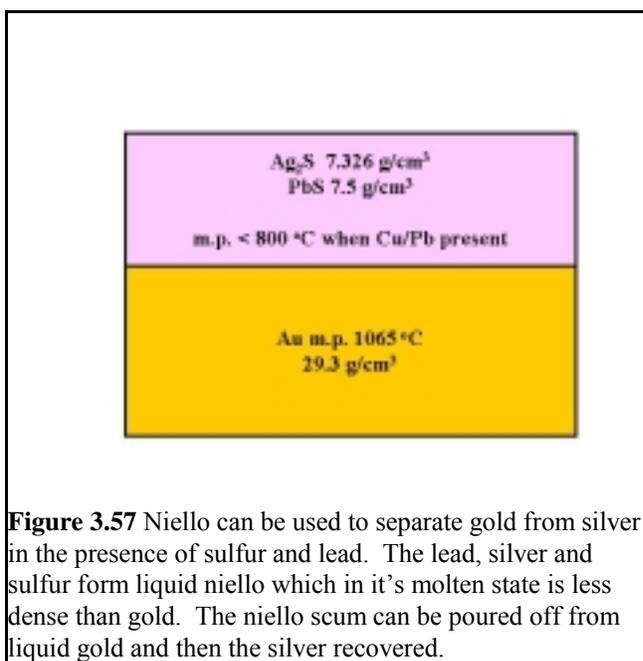
Niello was known in Kiev, Staraya Riazan, and Novgorod from 10-13th centuries (Palais, 1993, 56-59). Niello work experienced a major revival in the 16th -17th centuries. Its Russian masters included Vasilii Semenov (Moscow ca.1861) and Velikii Ustiug (1750-1760) (Snowman, 1953). Perhaps the most well-known of niello metalworkers was Faberge.

This master jeweler of the Russian Tsars in the late 1800s experimented in a wide variety of artistic forms, including the well-advanced Russian art of niello (Snowman, 1983).

Faberge is well known for his niello work, often associated with the royalty of Russian in the late 1800s. Many of his niello works can be found for sell in various art auctions, including those of Christies Auction house. Faberge was not the only Western European to experiment with niello. Another major worker in the material was Audemars Freres in Geneva. Many of his works are associated with pocket watches.

Scattered examples of niello work occurred elsewhere such as China (McElney). Niello, unlike other metal work in China, was a foreign introduction occurring approximately in the 8th century A.D. with some “true” (lead sulphide, copper sulphide and silver sulphide) niello identified from the T’ang dynasty .

Niello work in Thailand (Siam) is thought to have originated with the arrival of the Portugese in 1518 or earlier via India [Kellnar, 1993 #1990], [Samakhorn, 1982 #1991]. Thai nielloware techniques moved from Nakorn Sridhamray to the capital of Thailand, Ayudhya, where production of niello was mainly for the consumption of the royalty [Dittell, 2002 #1985]. Nielloware commonly known as Siam Sterling Silver, became a low cost easily affordable material under Mr. Somchitta Thiengham’s compnay, “Thai Nakon” in Bangkok which produced niello jewelry from the 1930s to 1997. Siam sterling silver



became very popular with U.S. servicemen stationed in the east shortly after WWII. Niello work was actively supported by the Thai government through the trade association of Thai Niello and Silver Ware Association of Thailand until 1997. Figure 3... shows an example of Siam Sterling silverware. One major difference between Thai Niello and those of Europe (Russia) is the use of the niello as the “background” in which the silver is framed as compared to the silver engraving effect used in Russian niello.

The craft of niello survive today in certain rural areas of Iran (Figures 3.55 and 3.56) and Central Asia (Figure 3.56B). In addition to the beautiful jewelry from contemporary rural Iran, there are somewhat cruder jewelry from Bukhara, Central Asian

(Figure 3.56C) and intricate workings on traditional jimbyas (knives) available throughout the Arabic world.

Niello jewelry is obviously a lead poisoning candidate but other sources of lead in jewelry exist such as the use of lead in the manufacture of clasps ([Harvey, 2003 #1989].

Toxicity of Niello

Niello is likely to be quite toxic based on the

fine powder used in the production of the jewelry. Although niello has not been identified as a source of lead poisoning, lead in jewelry from China and the Middle East has.

Purification of Gold from Silver Using Niello

The technology of fusing silver and lead sulfides works also to separate gold from silver (Figure 3.57). Silver and lead form miscible sulfides of low density (7.326 and 7.5 g/cm³, respectively.) The melting point of these sulfides, on their own, is 1100 °C and 1114 °C. When they are mixed together their melting point drops. Gold sulfides decompose at a much lower temperature (240 °C) than gold itself (1064 °C.) Liquid gold has a density of 19.3 g/cm³. As a result, upon heating, liquid pure gold settles to the bottom and the liquid sulfide material floats on top of it.

Theophilus describes the purification of gold from silver based on this process

Chap. 70 How to Separate Gold from Silver.

When you have scraped the gold off the silver put the scrapings in one of the small crucibles in which gold or silver is normally melted and press down a small linen cloth on top to prevent any of them being blown out of the blast from the bellows. Then put it on the forge and melt them. At once put in bits of sulphur proportionate to the amount of the scrapings and stir carefully with a thin piece of charcoal until the fumes cease. Immediately pour it into an iron mold. Then hammer it on an anvil, doing this gently so that one of that black which has been burnt by the sulphur may spall off, because it is itself silver. For the sulphur does not consume any of the gold, but only the silver which thus separates from the gold. Carefully save the silver, and again melt the gold in the same crucible as before and add sulphur. Stir it, pour it out, and break off whatever has become black and save it. Continue doing so until pure gold appears. Then put all the black that you have carefully saved into the dish made of burnt bone and ashes and add lead, and so burn it in order to recover your silver. If you want to keep it to use as niello, rather than burning it, add copper and lead to in the proportions mention above [III-28] and melt them together with sulphur.

Inadvertent Alloys: Metal Contamination: Implications for Recycling of Metals

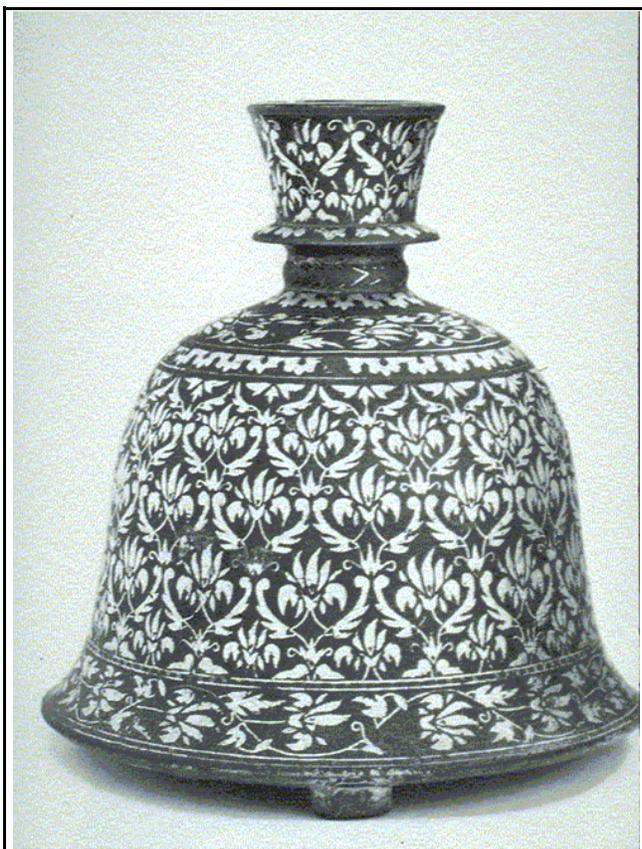


Figure 3.58 Bidri war, an alloy of copper and tin with large amounts of apparent inadvertent contamination of lead. Image source Strong, 1985.

Some of the alloys found in archaeological excavations are inadvertent mixtures of lead with other metals, apparently the result of remelting of scrap metal. One such example is shown in Figure 3.58. A second piece of Bidri ware from the same collection consists of 19.9% lead (Strong, 1985, p. 53). This is a type of metalwork known as Bidri ware. For the most part it consists of a zinc alloy, which is first inlaid with other, non-oxidizable, metals. Then the base zinc is oxidized to a black patina with a paste of ammonium chloride, potassium nitrate, sodium chloride, copper sulphate and mud. This form of metal work is named for the northern Indian town of Bidri, where it was first made in the 1600s or 1700s.

The high amount of zinc in the alloy means that pure metallic zinc must have been produced by the 1600s. Very precise control of temperature was exercised. Zinc melts at a relatively low temperature (419.58 °C) and boils at a low temperature (907 °C). A good deal of the zinc is lost in the metallurgical process. In contrast, lead melts at 327.502 °C and does not boil until 1740 °C. Zinc distillation was not patented in England until 1738 A.D. by William

Champion of Bristol.

The appearance of lead as an unintentional impurity from re-smelting has important implications for the establishment of economically viable metal recycling today. Most industrial and construction metals when recycled, contain variable amounts of different metals. Each type requires different techniques to produce a certifiable composition in the output metal. Aluminum recycling, on the contrary, has very nearly been a self-contained metal system from its introduction. Recycling of metal in aluminum cans carries little danger of introduction of a contaminate metal.

SUMMARY

Lead was used in the earliest phases of metallurgy because of its low melting point, its ease of processing in low temperature fires, and its resistance to rust. It was capable of alloying to Cu because both Cu and Pb adopt a face-centered cubic cell. When alloyed with copper, lead forms a lower melting phase. This helps control temperatures in the alloy crystallization process, creating a more fluid metal mixture. This alloy was apparently discovered independently and used in several different parts of the world (Mexico, Nigeria, and China). Both lead and silver adopt a NaCl ionic crystal structure (fcc), allowing them to alloy together as PbS and Ag₂S. This type of alloy, called niello, has been used as a black inlay to metallic objects. The alloys of PbS and Ag₂S allowed silver to be removed from a pure gold melt. Lead also shows up in a number of other alloys, sometimes inadvertently, causing contamination of metal feedstocks.

Chapter 3 Part II: Underlying Chemistry of Lead Metals & Alloys

In this section, we examine some of the chemistry that underlies alloy making. This chemistry allows us to understand why lead was added to bronzes and why leaded bronzes allowed metallurgists to create highly ornamented bronze faces.

Control of Gases

Casting of metal requires that the liquid metal be poured and that entrapped gases and/or those formed by the heating of the metal with its metal oxide impurities (e.g., oxygen), be allowed to escape from the mold. Copper, in particular, decomposes water and adsorbs gaseous hydrogen (H_2). Figure 3.59 (Society) shows the solubility of $H_{2(g)}$ in molten Cu, Sn, and Cu/Sn alloys. Notice that addition of Sn to the copper reduces the solubility of the gas in the liquid.

A second problem gas is water vapor. If O_2 is also dissolved in the metal, then upon cooling (solidification), the two gases, hydrogen and oxygen, can combine to form gaseous water. If the edge of the mold cools before the center of the cast, then the gas cannot escape and forms pockets within the metal, making the cast weak, spongy, and porous. Figure 3.59 indicates that the addition of tin to copper reduces the amount of hydrogen gas contained within the melt. A similar phenomena is observed when lead is added to copper. The addition of the second metal, because it removes hydrogen, results in a less spongy cast copper.

Lower the Energy Requirement

A second benefit of adding a second metal to the melt is the lowering of the temperature required to melt the copper. Just as when salt is used to de-ice sidewalks, the freezing point is lowered by dilution of the liquid. Freezing begins when the rate of the ice (solid) formation by accretion of liquid molecules to an incipient solid equals the rate at which the solid molecules escape and return to the liquid. The rate at which molecules encounter the incipient solid is determined by the number of liquid molecules in the

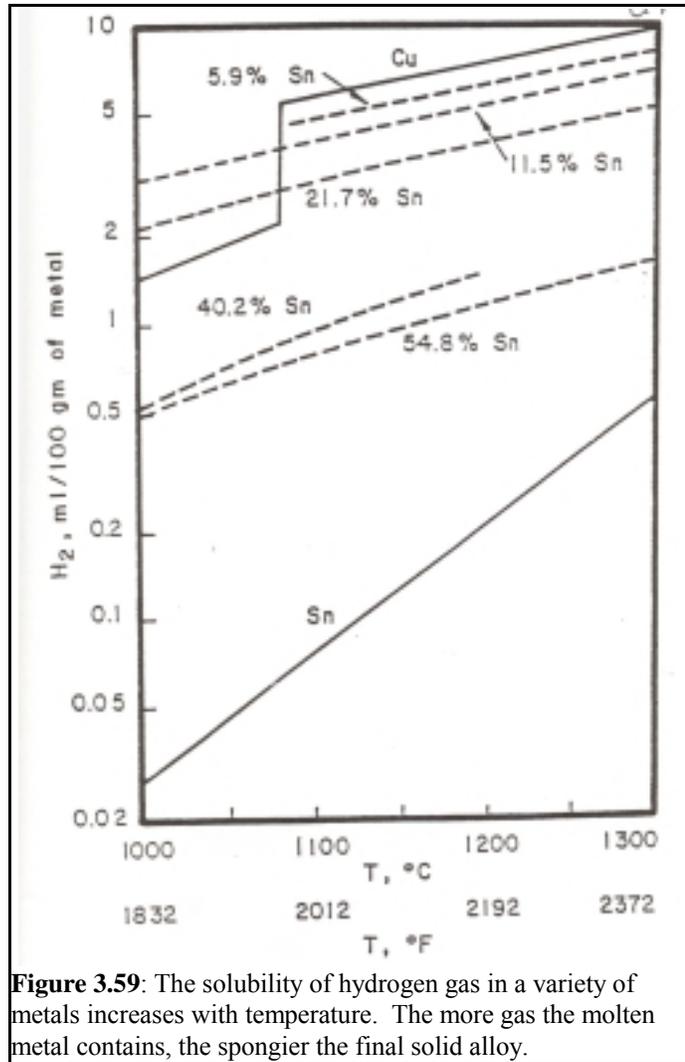


Figure 3.59: The solubility of hydrogen gas in a variety of metals increases with temperature. The more gas the molten metal contains, the spongier the final solid alloy.

volume of the liquid. Lowering the number/volume will decrease the rate of accretion. If this happens, the rate of dissolution will exceed the rate of formation and the solid will not form. The observed result is the presence of a liquid at a temperature at which ice is normally observed. A similar colligative phenomena is at work in metallurgy. The melting point of copper is lowered by the addition of secondary metals. Figure 3.60 shows how the melting point of copper varies as a function of the amount of additive. (A sample

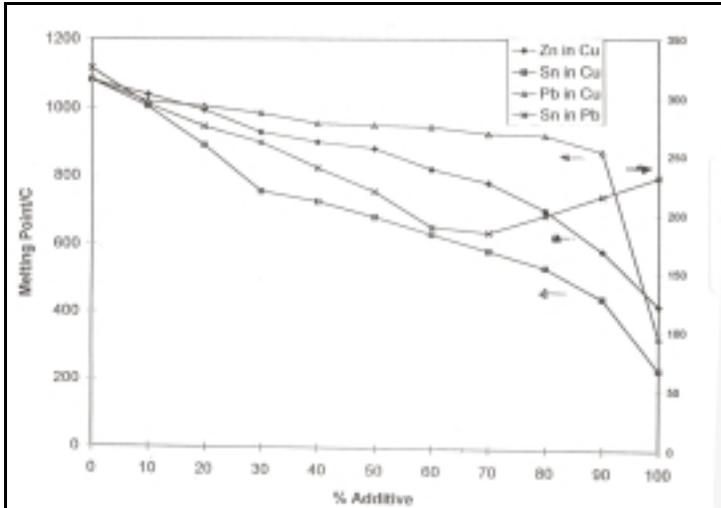


Figure 3.60: The melting point of a solid decreases when a second material is added.

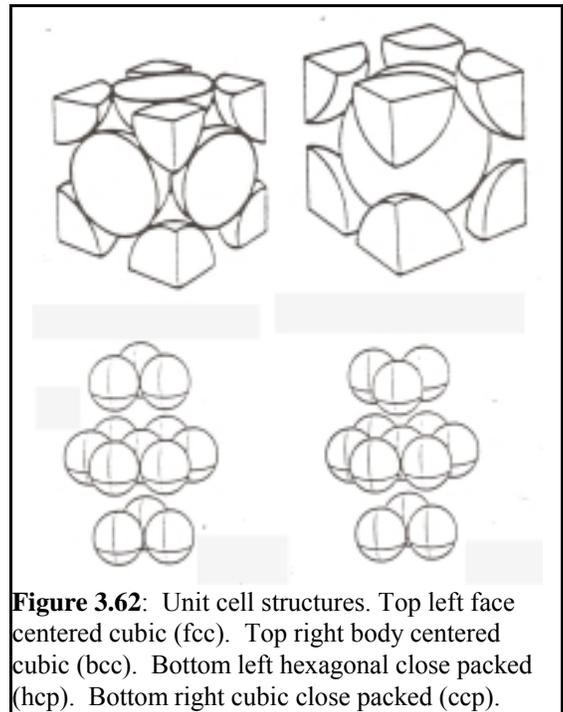


Figure 3.62: Unit cell structures. Top left face centered cubic (fcc). Top right body centered cubic (bcc). Bottom left hexagonal close packed (hcp). Bottom right cubic close packed (ccp).

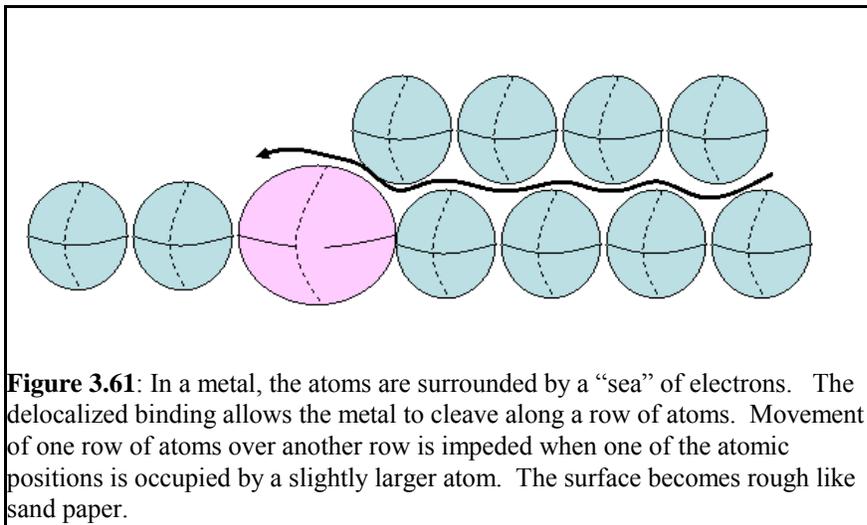


Figure 3.61: In a metal, the atoms are surrounded by a “sea” of electrons. The delocalized binding allows the metal to cleave along a row of atoms. Movement of one row of atoms over another row is impeded when one of the atomic positions is occupied by a slightly larger atom. The surface becomes rough like sand paper.

calculation related to the vapor pressure changes associated with copper (transition from liquid to gas) with addition of lead, a similar phenomena to the freezing or melting point changes, is shown in Examples 3.5 and 3.9. The decrease in the melting point makes metallurgy significantly easier. There is a drop from 1100° C to <800° C when 25% Sn is added. This moves the process into the range accessible with a hilltop furnace.

Control of the Final Solid Phase Structure

The third reason for adding a second metal to

copper is to exercise control over the hardness of the final product.

What causes the hardening of copper into bronze? Hardening is related to the ability to slip planes of atoms over the metal lattice. If the metal lattice is perfect, then an entire sheet of atoms should be able to translate across the surface, particularly if electrons are extensively delocalized within the metal (Figure 3.61). If, however, there is a defect in the lattice, then lateral motion will be more difficult. Defects

can be introduced either by the homogeneous substitution of other metals with slightly larger atomic size than the host atom into the crystal lattice.

These considerations give rise to three rules in the formation of alloys (Muller, 1993; Wells). The atomic radii of the two metals forming the alloy must be within 15% of each other, the two metals should both adopt similar crystal structures, and both should have similar electronegativity to avoid ionic compound formation. Na and K, while both adopting a body centered cubic (bcc) form (Figure 3.62, Table F.6) and

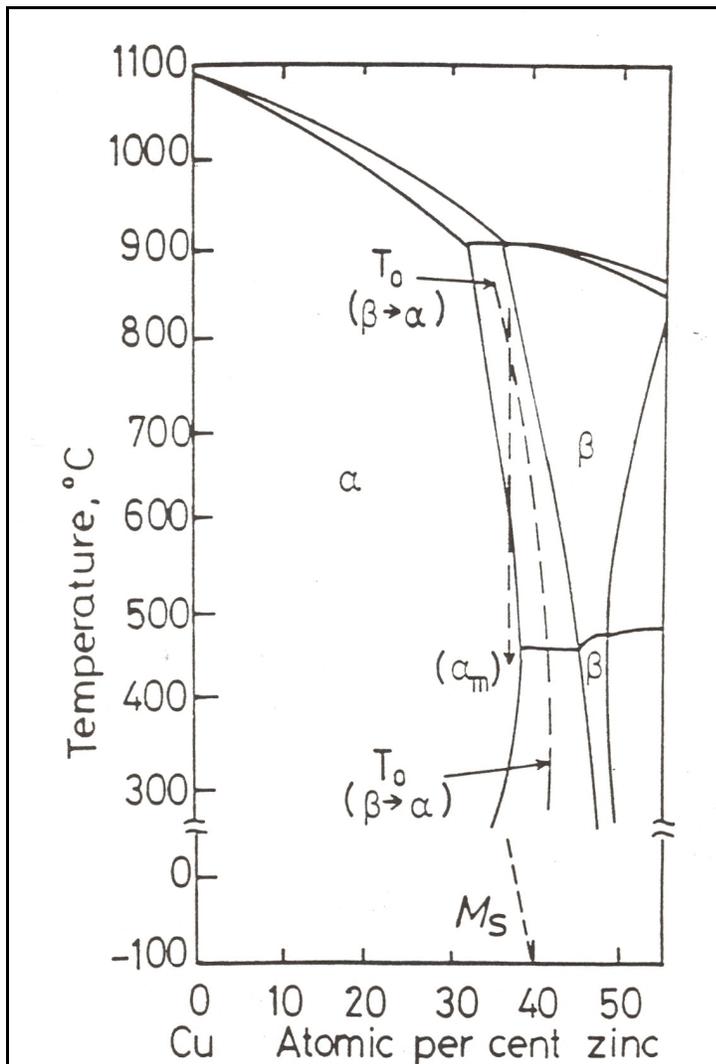


Figure 3.63: Phase diagram for copper with added zinc. As one reads across the bottom of the x axis a pure copper melt shifts in composition to 50% copper with 50% zinc. Plotted on the y axis is the temperature. Each particular composition can change in structure (see unit cell structures) as the temperature is changed. The various structures regions of stability are labeled. For example, copper prefers a face centered structure (Table 3.10), which is shown as stable as the α phase. This structure will be maintained until the metal melts at 1100°C. However, as zinc is added the face centered cubic structure coexists with a β , body centered cubic, structure. By about 40-50% zinc addition the β structure becomes dominate. Porter and Easterly, 1981, p. 353.

having similar electronegativity, do not form homogeneous solid solutions because sodium has a radius of 1.91 Å and potassium one of 2.35 Å. Cu and Ni form homogeneous alloys over a wide range, but Cu and Zn (brass) do not. The reason is that while all have similar electronegativity and similar atomic size

(1.28Å, 1.25Å, and 1.37Å, for Cu, Ni, and Zn, respectively) Cu and Ni both have face-centered cubic structure and Zn has a hexagonal close-packed structure.

Because of the different crystal structures of Cu and Zn, we might predict that a transition must occur in the structure of the alloy as Zn is added. Figure 3.63 shows a phase diagram for various crystal structures adopted by a Cu/Zn alloy as a function of the atomic percent Zn. Traversing from left to right at a fixed temperature, say 600° C, indicates that, as the amount of Zn is increased, the alloy undergoes several phase transitions. At the left where pure copper is present the composition is Cu, the phase is labeled α and a cubic closest-packed structure is adopted. (Cubic closest packed is the same as face centered cubic (fcc).) The next crystal phase encountered is the $\beta+\alpha$, followed by β (CuZn with body-centered cubic packing). As the amount of Zn is increased three more phases can be obtained: γ (Cu_5Zn_8 body-centered cubic with an expanded lattice and volume enlarged by 27); ϵ (CuZn_3); and η . Both of the latter have an Mg type structure, hexagonal closest packed (hcp) (Muller, 1993). The change in structure affects the metal electron bond and consequently the melting point of the alloy. Similar structural changes are noted for bronze (Cu/Sn alloy) (Figure 3.64). Another example of these structural change principles with composition is that of the Cu/Au alloy. A small segment of the stability diagram with temperature is shown in Figure 3.65. Figure 3.66 shows the different structural types adopted by the Cu/Au.

In summary, only certain elements form homogeneous solid solutions (alloys). As the % mixture is changed, the crystal structure changes, requiring a rearrangement of atoms that costs “energy”. A melt that cools can be “trapped” in one particular structure by careful control of the temperature during cooling or by cold working (hammering).

Trapping the Desired Structure by Controlling the Rate of Cooling

How can one control the crystal structure during cooling? The solidification of the melt can be considered as a series of chemical processes that begin

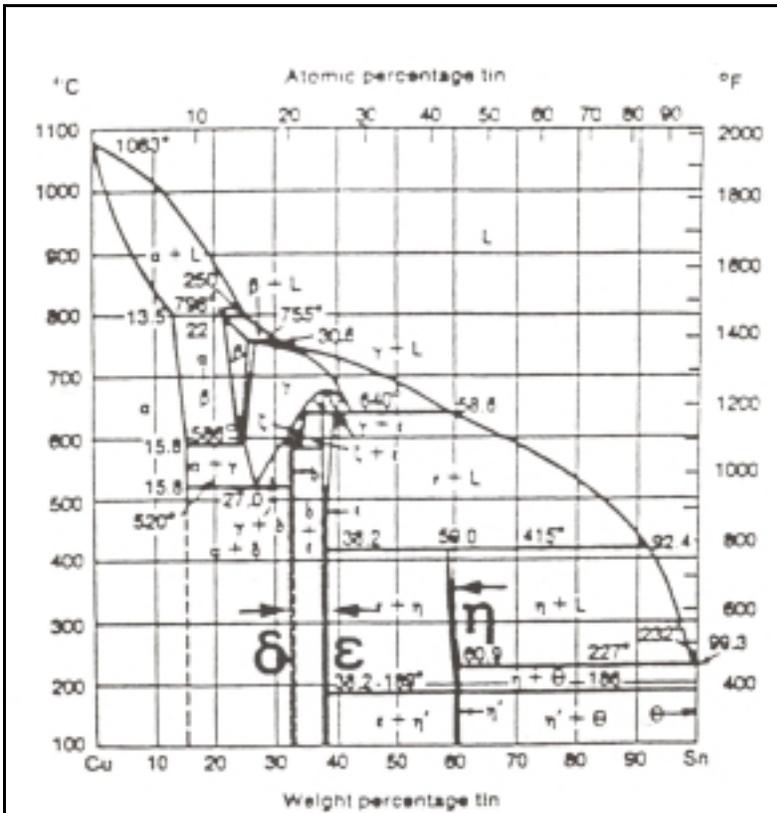


Figure 3.64: Phase diagram for copper and tin. As the composition of the metal changes from 100% copper to 100% tin, the unit cell structure changes. The temperature at which each unit cell melts is different, causing the overall melting point temperature to vary with composition.

with the nucleation of a new crystal. The relative diffusion of the liquid components to the nucleating sites increases the sites to larger size (Porter and Easterling, 1981, p. 191). The growth of the cluster depends upon the diffusion of the atom within the melt. The jump in Figure 3.67 shows how the atoms in a face-centered cubic structure must move apart to accommodate the motion of an individual atom jump and how this motion costs energy. The motion of an atom from one lattice point to another within the metal is known as self diffusion. Table F.5 shows the self diffusion of several metals, all of whom adopt a face-centered cubic structure (Figure 3.62), where Q/RT is the activation enthalpy for self diffusion (Brown and Ashby, 1980). The key point to notice in Table F.5 is that the enthalpy or “energy payment” is roughly constant. The “energy paid” depends on the type of structure adopted by the metal (Table F.7). The energy paid has the sequence $bcc < hcp < fcc$. This makes some sense if we look at the structures (Figure 3.62) and if we compare void volumes. The fcc requires a larger motion of atoms in the

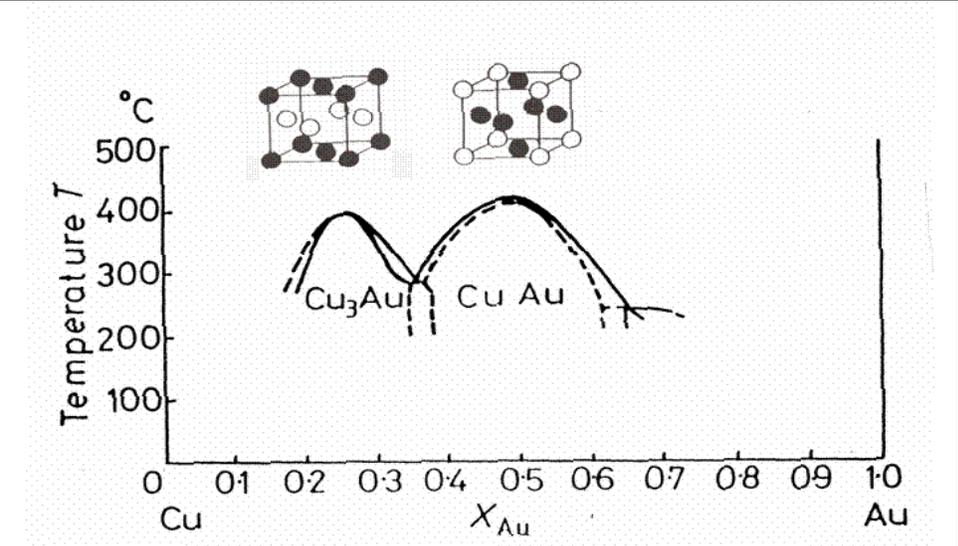
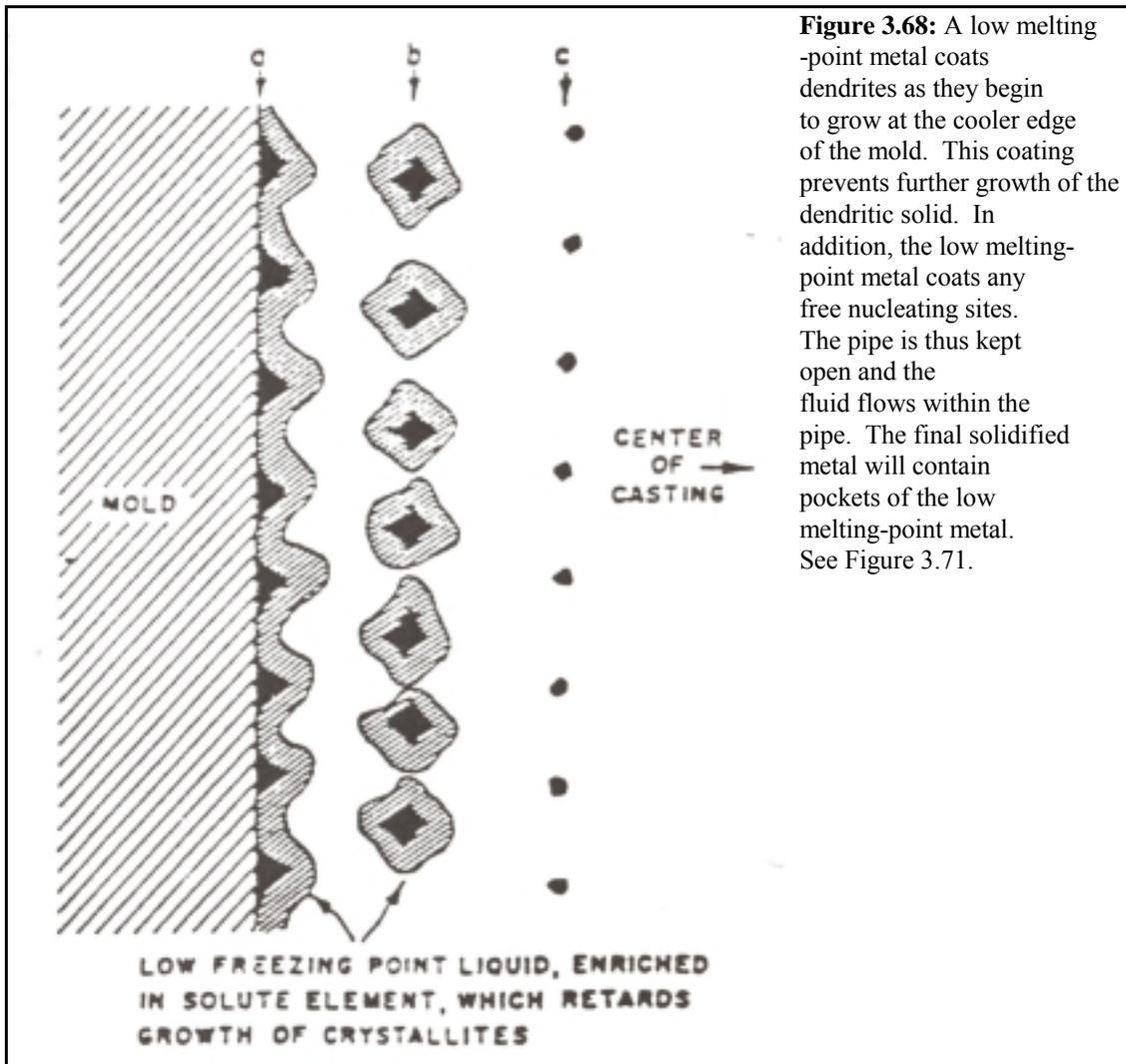
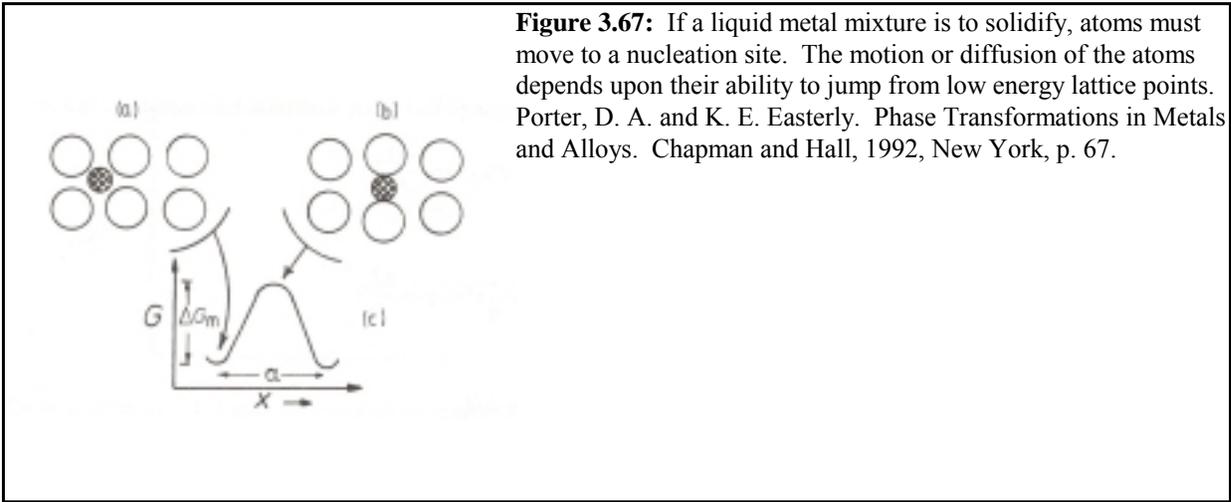


Figure 3.65: Relatively simple phase diagram for copper and gold, in which copper starts as a face-centered cubic structure. As gold is added, the structure changes to accommodate increasing amounts of gold atoms. See also Figure 3.66.

lattice to accommodate the jump of a single atom through the lattice. In other words diffusion is dependent upon the architecture of the site (i.e., distance to a new site), the number of vacancies, and the energetics holding the atoms together (Q).



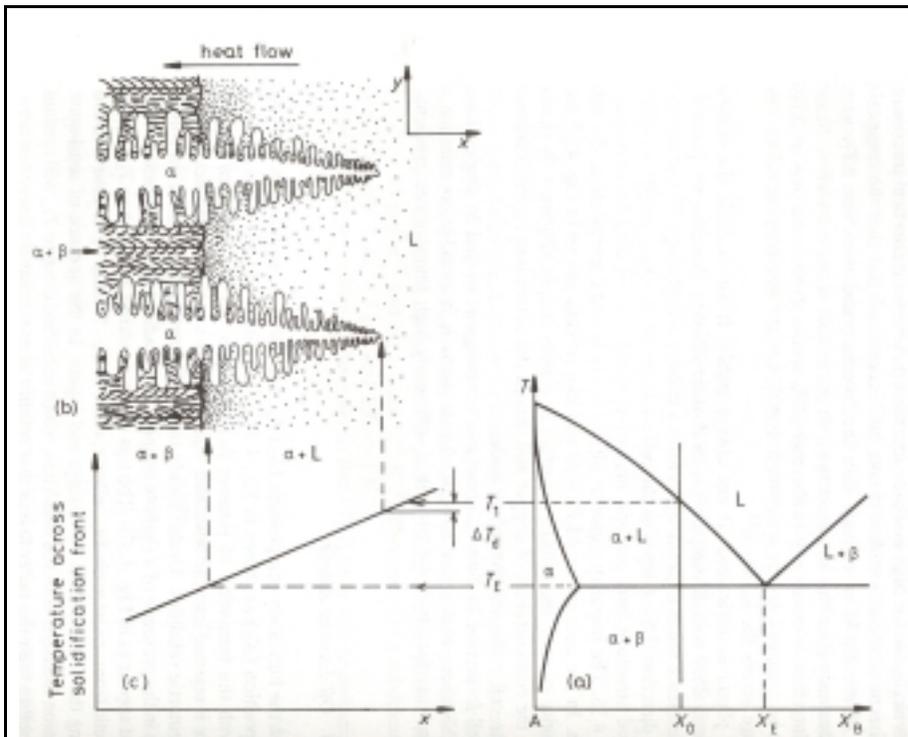


Figure 3.69: A melt starting with a composition X_0 (see right hand diagram) at temperature $> T_1$ homogeneously fills the mold. However heat flows from the mold to the edges, causing the temperature to fall near the edges (diagram lower left hand corner). This corresponds to a vertical drop along the X_0 composition in the figure at the right. When the temperature falls below T_1 , homogeneous liquid, L , is in equilibrium with the solid metal in a unit cell structure, α . The α solid precipitates, initiating a dendritic structure (diagram upper left). At areas even closer to the outer edge of the mold, the temperature is even lower. Moving down the X_0 line in the right hand diagram, it becomes apparent that two solids can coexist with different unit cell structures, α and β . These solids fill in between the α -containing dendrites. Porter and Easterly, p. 230.

Returning to the problem of alloy formation as a function of temperature, we now see that we need a nucleation site (where a crystal initiates) and diffusion to that site to cause crystal growth. When our melt cools in a casting, we have temperature gradients across the melt. This means that different sizes and numbers of crystals will form and have different rates of diffusion as they form. This is termed a non-isothermal condition. Consequently, one part of the melt may have a rapid nucleation and diffusion of component A and another part of the melt a rapid nucleation and diffusion of a component B. Where these two places meet, there is an unequal composition of the alloy. The early metallurgist was required to master precisely these difficult systems in the casting of alloys.

When these temperature and concentration

gradients originate from the surface, columnar structures can develop (Figure 3.68). In other cases, where concentration is changing more rapidly than temperature, dendrites (fingers) can be formed (Figure 3.69). The dendrites create a problem in mold casting of the metal because they cause obstructions that slow down the flowing liquid in the center of the mold. Coarse dendrites impede the flow of liquid to the outer edges (Fasoyinu et al.). Figures 3.47 and 3.48 show images of a dendritic structure formed by the precipitation of pyrolusite by diffusion into a sandstone layer and in a geode. The formation of dendrites occurs similarly in a tin copper alloy. Lead is used to prevent dendrite formation, that is, to increase fluidity and moldability. A typical casting metal is that of the English "leaded gunmetal" (Higley et al., 1971; Mills and Gillespie, 1968). British standard alloy LG (leaded gunmetal) 2 is

composed of 85% Cu, 5% Zn, 5% Sn, and 5% Pb. LG3 is composed of 86% Cu, 5% Zn, 7% Sn, and 2% Pb. LG 2 flows more easily than LG3.

Extra Lead Prevents Dendritic Growth

Figure 3.70 shows why liquid lead is useful in the solidification of a copper alloy (Society, 1984). The figure shows the copper lead phase equilibrium diagram (Marcotte and Schroder, 1983). Pure copper exists as an α phase, pure lead as a β phase. Any amount of mixture forms an $\alpha + \beta$ phase at all temperatures up to 326°C . At 326°C the lowest melting temperature is encountered, giving rise to the copper-lead eutectic. (*Eu*- Greek for "beneficial" or "derived from a specific substance"; *tektos* means

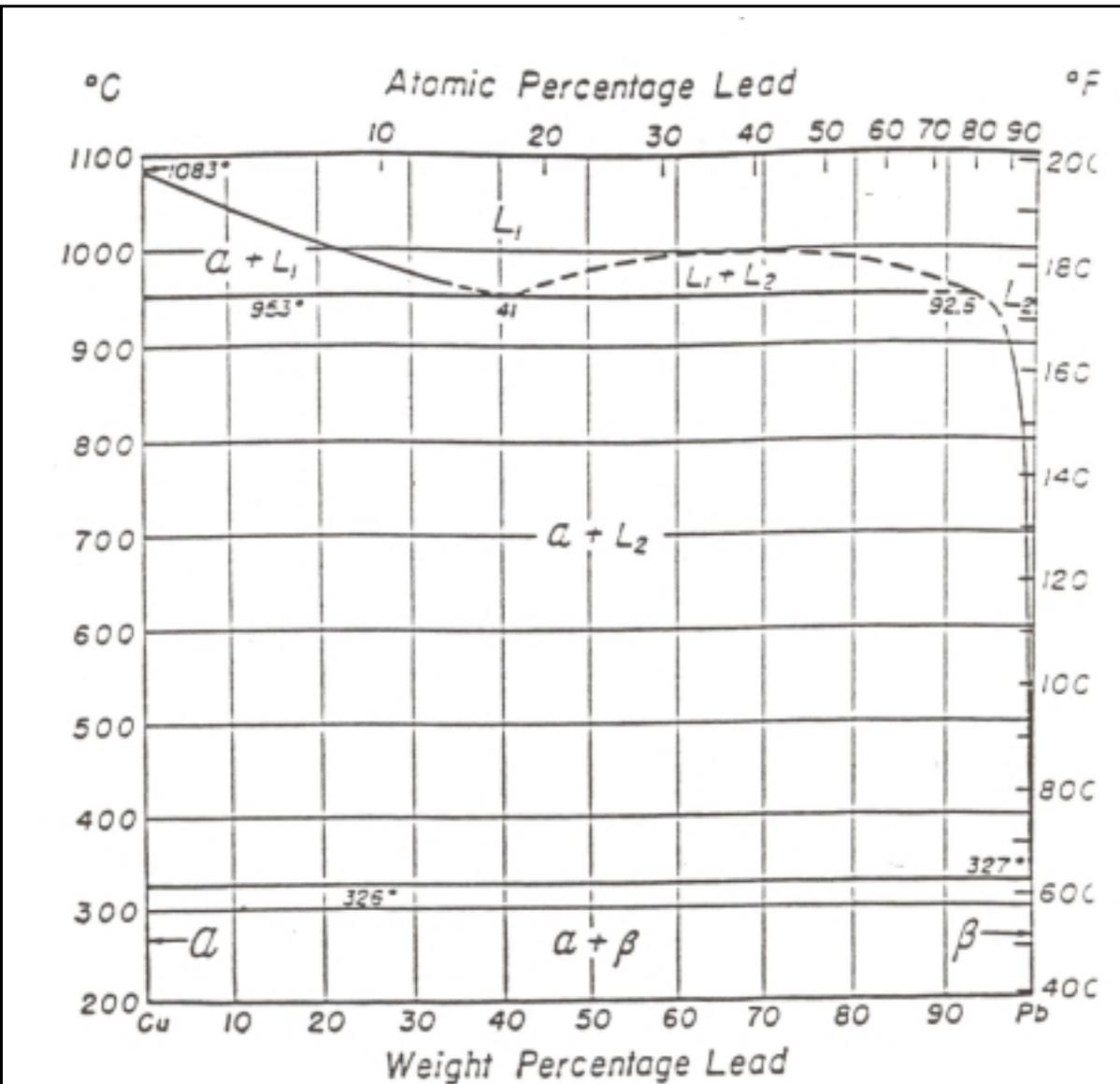


Figure 3.70: Phase diagram for copper lead. Lead lowers the melting point of copper slightly if a small amount is added to the copper. More importantly, the mixture remains in a partially liquid phase for an extended temperature range. This extended phase allows liquid to coat solid particles and to keep the material fluid in injection into a mold. It also means that with pressure-induced temperature increases, the metal forms liquid states that allows metal to move on metal.

“melted”). Between 326°C and 900°C, Cu exists as an α phase in liquid lead. Above 953°C, Cu exists in a liquid copper phase. At higher lead composition, liquid lead and liquid copper coexist. This has implications for the formation of copper solid on cooling. The melt is coolest at the edges, and hottest inside where the melt was injected, leading to the dendritic growth described above. The dendrite crystal growth is slowed down by the presence of a low freezing point liquid (lead), which forms a coating

around the growing crystal edges and even isolates crystal formation from the dendrite into small mobile islands. Lead can be seen as ‘droplets’ in many bronze castings in scanning electron micrograph (SEM) images (Figures 3.71 and 3.72). As a result, injection ports stay open long enough to be able to inject the liquid metal all the way to the outer edge of the mold. A similar process can be envisioned for the copper-tin-lead ternary system (Hofman, 1970, 151-

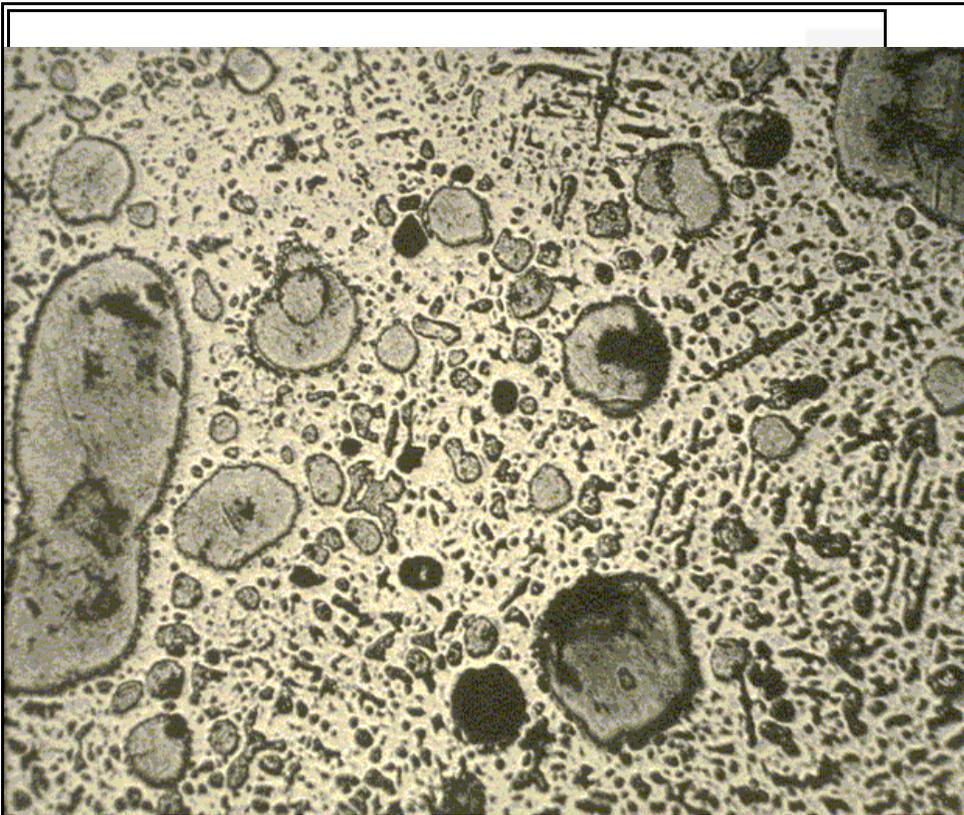


Figure 3.71: Scanning Electron micrograph of lead globules within a bronze material.

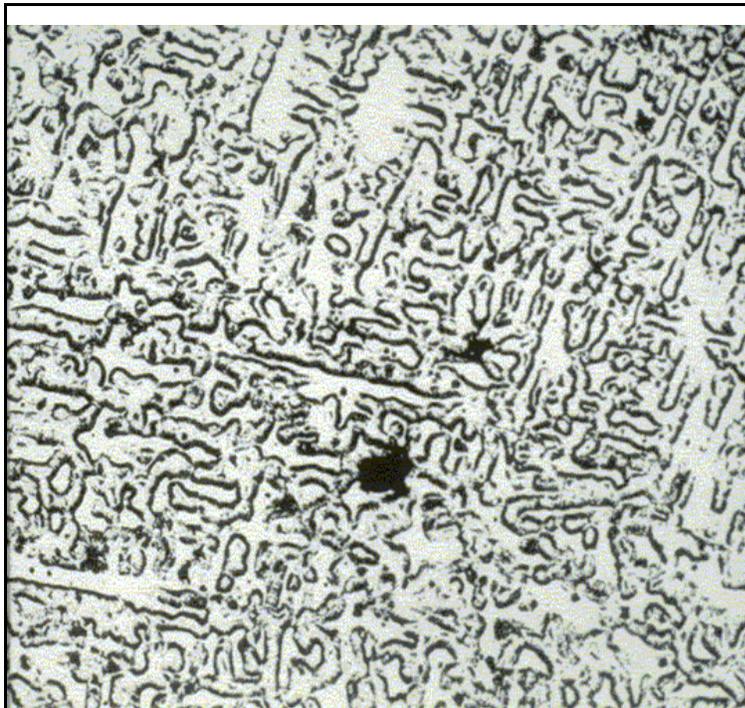


Figure 3.72 Scanning Electron Micrograph (SEM) showing dendritic growth of the main metal but also large black dots of pure lead metal.

153). The ternary system has been reviewed by several workers (Chang et al., 1979, p. 631-642)

Another contemporary alloy that uses lead is “red brass”, a Pb-Cu alloy used primarily in plumbing or in naval applications (Table F.4). Its 4-8% lead composition makes it easy to machine. However, there is a fear that the lead smeared across the surface during machining could be leached. Replacement of lead by Bi has been proposed (Whiting and Sahoo, 1995). Bi could substitute because of its properties, economics, and toxicology. It can serve the same purpose as lead by spreading

around the copper dendritic grain as it grows. Figure 3.73 shows the Cu/Bi phase diagram. The eutectic is reached at 270° C, the point at which there is a solid copper phase embedded in the liquid Bi. When the total liquid system cools (above 1084° C), the nucleating copper will be within a sea of low melt Bi.

In summary, the use of lead facilitates continued flow of the alloy. Lead is eliminated from the alloy formation of Sn and Cu and thus forms pools that coalesce around dendrite formation. In effect, the lead forms an internal grease that prevents the continued growth of the dendrite and facilitates flow of the nucleating sites away and to external edges of the mold. Lead has been intentionally added to many bronzes for several thousands of years. It has been put primarily into bronzes that have a high amount of surface detail (and thus flow into crevices) and in materials that will be machined or that must sustain some amount

of deformation. Microscopic analysis of many ancient bronzes, including Chinese ones, shows dendritic growth of Cu/Sn, with concentration of low freezing point composition at the coolest dendritic edges leading to segregation of phases, and encapsulation of the dendrites (Oya et al., 1974).

An Example of Alloy Phase Control: The Making of Mirrors

Both Etruscan and Chinese mirrors have a surprisingly similar composition of both tin and lead. The δ phase of Cu and Sn occurs between 19 to 27% Sn, a far higher composition than for bronzes discussed earlier. These high-tin bronzes are far too brittle for warfare or agriculture. The δ phase is also known as silver white, and is the optically active Cu_3Sn_8 . (The optical properties of this material will be explained in Chapter 5.) The average composition of a Chinese mirror is 70% Cu, 25% Sn, and 5% Pb (Chase and Franklin, 1979, p. 11). The high Sn bronze in Chinese mirrors was cast and slowly cooled to develop a two-phase microstructure of α Cu and δ Sn (Taube et al., 1995). These mirrors had a typical lead content of about 5% (Yao and Wang, 1987). Roman mirrors also have the δ Cu_3Sn_8 phase (32.6% Sn), formed from the $\alpha + \delta$ eutectic on isothermal cooling.. These too have lead present, observable as globules upon surface imaging. Perhaps as the δ phase cools, it concentrates the Sn, leaving behind a richer Cu α phase in a sea of lead. Lead content of the final product is about 6%. The presence of lead seems to be important in stabilizing the separation of the δ phase (perhaps as heat conduction?)(Yao and Wang, 1987). While lead does not interact with the other phases, it affects the crystallization kinetics. This possibility is supported by a historical analysis of the recipes of the mirrors. According to the analysis, lead was added in excess of 5%, the remaining 5% was

present because of entrapment. The *Six Receipts of Chin*, recipes for bronze dating to 10th century B.C., give explicit formulations of various bronzes (Chikashige, 1936) (see Table 3.14). The constancy in lead composition across cultures thus cannot be used as an argument for diffusion of technology. Clearly the technology was driven by the chemistry of the melt, not by the idea of adding or not adding particular proportions of an ingredient to it.

Chinese mirrors and the technology for making them were exported to Japan. Analysis of these Japanese mirrors shows that they have very similar lead composition, suggesting that the technical ability for manipulating the alloy was high (Mabuchi et al., 1985).

Chapter 3: Homework

1. Outline the main time periods for use of lead as a sculpture in European art.
2. Why is Messerschmidt, a minor sculptor, of interest to us?
3. Why are lead projectiles better weapons than small stones?
4. What is the concentration of lead when a constant, 0.01M, concentration of monophosphate is fed through your water supply?
5. Which metal is most likely to rust, Pb or Fe? Do you have enough information to comment on the rusting rate for each of the at which se two metals?
6. When did lead baptismal fonts come into vogue in England and why?
7. What was the advantage of lead as a roofing material?
8. Name three historically and architecturally significant buildings made with lead roofing.
9. What are aesthetic properties which make lead an attractive roofing material?
10. What drove the historical change from pure copper to copper alloy objects?
11. What is the composition of a “typical” brass? Of a “typical” bronze?
12. What makes copper become harder it is alloyed with Sn or As?
13. Both Etruscan and Chinese mirrors were made with 5% lead. Does this fact support the argument ithat metallurgy diffused from west to east?
14. Why are pre-Colombian Mexican bronzes occasionally leaded?
15. Was the route for technology transfer

Table 3.14: Composition of Chinese Bronzes

Six Receipts of Chin , 10th Century B.C

<u>Article</u>	<u>% Cu</u>	<u>% Sn</u>
Bells	86	14
Axes and hatchets	83	17
Halberds and spears	80	20
Swords	75	25
Knives and arrow heads	71	29
Mirrors	50	50

- overland or by sea for the Americas? What does the answer imply for the overall transmission of agricultural practices?
16. During casting, what has to be controlled when the metal is cooled?
 17. Why is the metallurgy of pre-Columbian South America of interest to environmental scientists?
 18. Was metallurgical development in Nigeria “independent”? Why did it take so long compared to development in Mesopotamia?
 19. Did the Nigerians use lead in their bronzes? For what purpose?
 20. True or False: Chinese Bronzes developed independently of Mesopotamian ones. Why or why not?
 21. What **kinds** of Chinese bronzes were leaded?
 22. Could Ag_2S be inlaid into Ag by heating the silver object?
 23. Why add PbS to Ag_2S for inlaying on Cu, Ag, or Au?
 24. Why was niello used extensively during the period of mass migrations in Europe?
 25. How is gold separated from silver using sulfide chemistry? What temperature does the melt need to achieve? Can it be reached with a hillside furnace?
 26. What makes recycling of industrial scrap metal economically problematic in modern times?

Problems Suitable for Chemistry Students

27. Write out the electron configuration of Pb^{2+} . What is the most significant feature of this configuration in determining lead chemistry?
28. What chemistry controls the steps (melting, molding, fixing) of an object manufacturing process?
29. Write out the reaction of lead with oxygen. What is the free energy Pb metal’s reaction with oxygen?
30. Contrast your answer in 29 to that of the reaction of iron with oxygen.
31. If you are trying to manipulate Cu at 1150°C , what amount of Sn would give you a significant reduction in H_2 gas? Define “significant” as you prefer.
32. What are the three rules that control alloy formation?
33. Will Cu and Zn make good alloys over a large compositional range?
34. Can Na and K be alloyed easily?
35. Can Na and Cu? Why or why not?
36. How does the crystal structure affect the melting point?

37. Which is easier to melt: fcc, hcp, or bcc?
38. What is the trend in melting points for the second column of elements in the periodic chart?
39. When casting, would you prefer to have columnar or dendritic structures form? Why?
40. What does the addition of lead do to the casting process?
41. Define eutectic.
42. What would be a good replacement for lead in the temperature control of the melt?

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