

# Chapter 2

## The Introduction: Man Asks Lead Out Mines and Mining

*The bellows are burned, the lead consumed of the fire;  
The founder melteth in vain; for the wicked are not plucked away.  
Reprobate silver shall men call them  
Because the Lord hath rejected them.*

Jeremiah 5: 29-30. (610 B.C.)

**A**lthough lead has been shown to occur in abundance near early human habitation, exactly how easy was it for early mankind to separate lead from the rock ore? The environmental chemistry of the arctic ices (Figure 1.3) gives a record of major lead production times in human history. It is evident that lead was extracted (mined) from early times and that a substantial amount of the world lead burden began with the discovery of a process called **cupellation**, accelerated with the advent of silver coinage during the Greek civilization, and reached massive proportions during the Roman civilization. Interestingly, the advent of large scale mining in the New World did not contribute to the same amount of lead pollution as earlier processes. Why should this be so?

### Part I: History, Art, and Technology of Ore Extraction and Processing

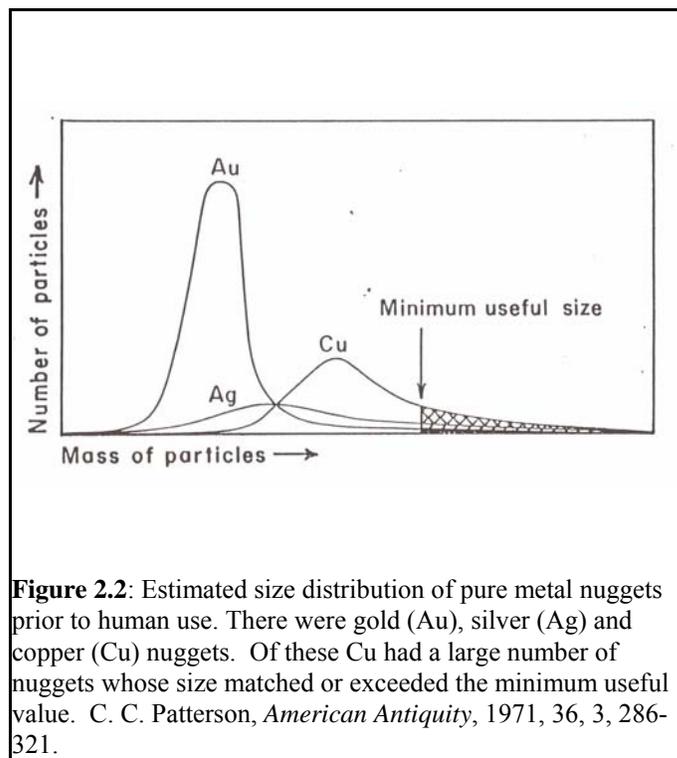
#### Found Elements

The first seven metals discovered by humans cluster around the end of the d block in the periodic table. Some of these are termed “found” metals because they are stable upon surface of the earth. “Found” metals include the “noble” or coinage metals found near the end of the d block of the periodic table

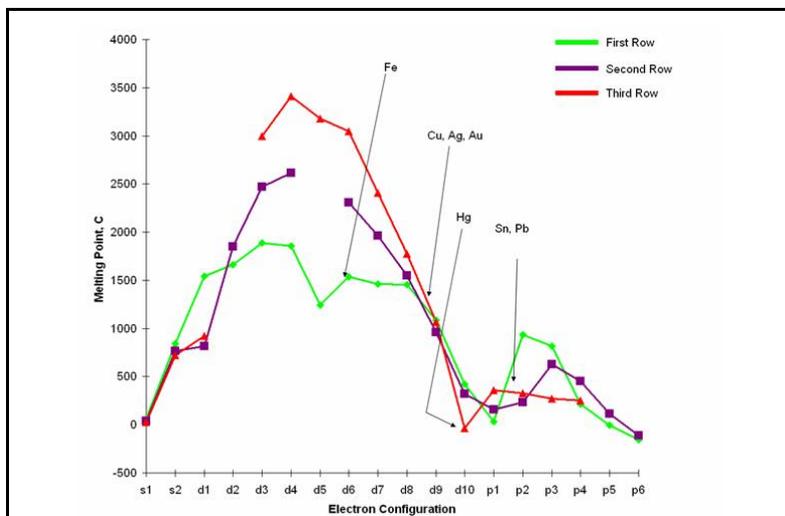
|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |  |  |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|--|--|----|
| H  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |  |  | He |
| Li | Be |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |  |  | Ne |
| Na | Mg |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |  |  | Ar |
| K  | Ca | Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |  |  |    |
| Rb | Sr | Y  | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I  | Xe |  |  |    |
| Cs | Ba | La | Hf | Ta | W  | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |  |  |    |

**Figure 2.1** Periodic table showing the first 7 metals known to man. These metals, with the exception of iron, all occur near the end of the d block.

(Figure 2.1). Gold and copper were likely known and used



**Figure 2.2:** Estimated size distribution of pure metal nuggets prior to human use. There were gold (Au), silver (Ag) and copper (Cu) nuggets. Of these Cu had a large number of nuggets whose size matched or exceeded the minimum useful value. C. C. Patterson, *American Antiquity*, 1971, 36, 3, 286-321.



**Figure 2.3:** The melting points of the elements as a function of their position in the periodic table. The first metals known to mankind, with the exception of Fe, have low melting points because they are near the end of the d block. Data Source: CRC Handbook.

as found. Silver, on the other hand, occurs in such small size that its “found” usefulness was limited. (Figure 2.2).

The coinage metals are found in pure form because to achieve a filled or half filled shell or subshell configuration, they would need to lose at least three electrons. On the other hand, by promoting two electrons from the “s” orbital, they can achieve a stable filled d block. These found metals can be melted, although the melting temperature is higher than that attained by a simple campfire (500-600°C) (Figure 2.3).

### Melting Point

The melting points of all early use metals are low due to their position within the periodic table (Figure 2.3). The melting points follow obvious trends in the periodic chart. Melting points should be related to the ease of “shoving about” the electrons. The attraction between the electron and the atom center is higher when a single electron occupies the orbital. A good example of this principle is the rise in melting point as the d orbital begins to fill. (Keep in mind that d orbitals can sometimes use s electrons in filling). Since initially all 5d orbitals are identical, electrons prefer to take all available orbitals (single occupancy). After the fifth electron is added, double occupancy begins, less metallic bonding is possible, and the melting point begins to decrease. Note the low melting

point of lead, especially compared to that of iron.

The melting point, however, is an indication only of the use of the purified metal, not of the processes required to turn the ore into the metal. With the exception of the so-called noble metals (copper, silver, and gold), metals do not exist in significant quantity in nature as the pure element.

Conversion of rocks containing a particular metal requires several metallurgical processes. One process is smelting, defined as the heat treatment of an ore to separate the metallic portion and then reduce it. The smelting results in “pig” metal. Refining involves further concentration of the pig. Pig lead from Missouri lead mines contained 0.007% silver while refined lead from the same mines contained 0.005% silver (Hahn, 1924) p. 11-14.

### Purifying the Elements

Once a mineral has been removed from the earth it still must be purified. If the mineral is exceedingly pure (large galena or ceruse) chunks it may be possible to directly process the mineral by heat treatment. Oxidized ionic salts of lead, for example,  $PbCO_3$  (ceruse or cerusite), need to be heated to break bonds and simultaneously reduced to form lead metal. Carbonate and nitrate salts, in the presence of oxygen, lead to the formation of lead oxide. In the presence of carbon monoxide, lead carbonate is decomposed to lead and carbon dioxide. These reactions (Example 2.1) show that ceruse can be easily decomposed to  $PbO$  with the intense heat of a well built fire. However the reduction of lead cation to lead ion requires a “reducing” heat (made possible by the absence of oxygen, or by large amounts of charcoal).

Historically, once the surface or oxidized ores were depleted, subsurface sulfide ores were utilized. Sulfide ore cannot be utilized unless the metal sulfide bond is broken. It should be chemically possible to convert galena,  $PbS$ , to the ore even at campfire temperature (Example 2.2). The spontaneous reduction of galena can occur at all temperatures above 0°C, in contrast to copper which is non-spontaneous until the temperature exceeds 922°C. This means that the reaction for lead will occur given enough time and

**Table 2.1: Chemical Properties Relevant to Smelting**

| <u>Material</u>                                      | <u>Melting Point, °C</u> | <u>density g/cm<sup>3</sup></u> |
|--|--------------------------|---------------------------------|
| Pb   | 327.4                    | 5.75                            |
| Al <sub>2</sub> O <sub>3</sub>                       | 2072                     | 3.765                           |
| CaO  | 2614                     | 3.25                            |
| MgO  | 2852                     | 3.58                            |
| SiO <sub>2</sub>                                     | 1610-1723                | 2.29 to 2.6                     |
| Ca <sub>3</sub> SiO <sub>5</sub>                     | 2130                     | 1.718                           |
| Ca <sub>2</sub> SiO <sub>4</sub>                     | 1900                     |                                 |
| CaSiO <sub>3</sub>                                   | 1200-1540                | 3.27                            |
| CaAl <sub>2</sub> O <sub>4</sub>                     | 1600(decomp)             | 2.981                           |
| 2Ca·Al <sub>2</sub> O <sub>2</sub> ·SiO <sub>2</sub> | 1590                     | 3.048                           |
| CaAl <sub>2</sub> Si <sub>2</sub> O <sub>3</sub>     | 1555                     | 2.765                           |
| Al <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub>     | 1545                     | 3.247                           |

Data Source: CRC Handbook

isolating any desirable element is to remove these most abundant materials. This is accomplished by the process of smelting. In smelting the ore rock removed from the mine in the presence of other rocks is broken, sorted, crushed, ground and water sorted. The remaining material is still high in the O, Si, Al, Fe, Ca, Na, K, and Mg. To separate the ore from these materials the crushed ore is smelted. Smelting involves high temperature processes which melts everything. By carefully controlling the mixture, Ca, Al, and Si can be made into a liquid of lower density than the metal ore. The heavier fluid can be pulled off at the bottom of the melt, as a purer metal mixture of the metal of interest (lead) with impurities of Cu, Bi, Al, S, Fe, Sb, As, Zn, Ag, etc. The less dense liquid is discarded as “slag”. Table 2. 1 gives the melting points and densities of a variety of Ca, Al, and Si mixtures as compared to lead. You should note that the temperature at which the Ca/Si or Ca/Al/Si melts depends very much upon the exact compound. Control of the mix to get a material melting at a low temperature is important.

The denser metal pulled off at the bottom is not yet pure and is called “pig” lead. The pig lead can be furthered purified to isolate silver by a process called cupellation.

### Coinage

Although lead was discovered very early in human history, its use and dispersion were greatly increased by developments in silver production.

Silver production in the western world increased dramatically with the advent of coinage as noted in Figure 1.3. The large spike in lead production at 700-600 B.C. occurs at the advent of coinage. Coinage dates to the time of Lydia (now Turkey) although its widespread adaptation was driven by the Greek islands bordering Lydia. The first Lydian coins were struck of electrum, a naturally occurring alloy of copper and silver available in Lydia. King Croesus (c. 560-547 B.C.) struck coin of electrum and was the first to adopt bimetallism using both gold and silver coinage. Archaeological evidence for separation of gold from silver exists at Sardis. Art history data pushes the inception of coinage back to the mid 7<sup>th</sup> century B.C. (Burnett, 1987) (p. 4).

The Persians who followed the Lydians

temperatures exceeding 0°C.

This chemical reasoning predicts that lead can be formed from PbS at temperatures reached by a kiln, a hypothesis advanced by Tylecote but discounted by Patterson as too difficult a process (Tylecote, 1962), p. 76. It is easier to obtain lead ore by “roasting” the galena (PbS) to form the oxide (PbO). The roasting reaction begins by 500 °C and is complete by about 600 °C. The sequence of reactions is quite complex, however, the overall reaction is the reaction of lead sulfide with oxygen to form metallic lead and sulfur dioxide (see second part of chapter). These reactions occur at campfire temperatures. A single fire could be used for both processes in an open air fireplace. In Yorkshire an open air fireplace near the top of a hill (for good wind pull) a fire was built and crushed rock containing PbS added. PbS was roasted to PbO and over the top of the roasted metal more fuel and ore was added. The lower part of the fire became a bed of charcoal which served to reduce the lead with relatively pure metal running off the bottom ((Raistrick, 1975)

Rarely is cerusite or galena found so pure. The rock containing these minerals is often mixed with other materials. As a consequence lead has to be removed from cerusite and galena in the presence of a large number of elements found in the Earth’s crust. The crust consists predominately of oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. The abundance of these elements derives from the Earth forming processes discussed in Chapter 1 (Table B.8 and Figure 1.13). The first step in



**Figure 2.4.** A lead with a horse motif from the 2<sup>nd</sup> or 3<sup>rd</sup> century A.D. of the Deccan, India. Collection of the author.



**Figure 2.5:** Lead coin, Sinkiang, east of the Bactrian Central Asian states founded by Alexander the Great. (Author's collection).

continued to produce gold coins but the Greeks almost exclusively used silver for their coinage. Greek coinage was exported throughout Asia Minor via the conquests of Alexander the Great. The Seleucid remnants of the Alexandrian empire in central Asia continued the minting of Greek style coins, including those from Bactria (Central Asia) in 285 B.C. As the empire fell into separate kingdoms independent royal mints evolved in Central Asia around 200 B.C. To the south of the Alexandrian kingdoms was the empire of the Mauryans which occupied most of continental

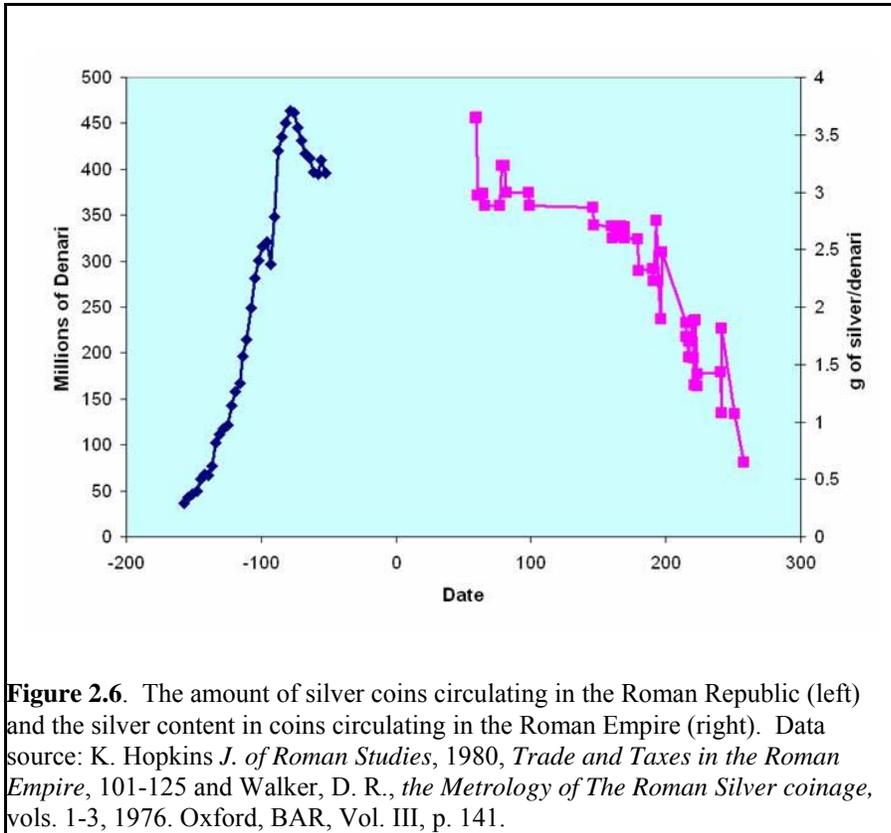
India. With the disintegration of Mauryan empire of Asoka (~300 B.C.) northern India was drawn under the influence of the Alexandrian state of Bactria which minted bilingual coins in Greek and Hindi.

Bactrian control of Northern Indian was altered by invasion of Scythians who were pushed out of central Asia by the nomadic tribes in search of pasture who were pushed west by the Han of China. These Scythians were known as the Sakas. The Sakas were in turn pushed further south into India by the Parthians (Pahlavas) eventually coming into conflict with the peoples of the Deccan area of South East India by about 78 A.D.

The Deccan had also been part of the Mauryan Empire of Asoka. The fall of the Mauryan Empire began the rule of the Satavahanas for about 400 years (~200 to 200A.D.) in the Deccan. Various Andhra principalities were unified under the Satavahanas. The Satavahanas issued coins of copper and billon (an alloy of silver and copper containing less than 50% silver), lead and potin (an alloy of copper, zinc, lead, and tin) (Sircar, 1968). The fall of the Satavahana after defeat by the Saka Rudradamana left invaders and local rulers to carve out their own kingdoms, many of which issued their own coinage (e.g. the Ikshvakus, ruled 234-332 A.D., Deccan, (Sircar, 1968) (p. 150). Similarly, political turmoil in southern Indian is known historically by the chronology of coinage, including lead coinage of the Chuta and associated groups. Figure 2.4 shows one such Indian lead coin which apparently dates from the 2<sup>nd</sup>/3<sup>rd</sup> century of S. E. Deccan. A similar horse marked lead coin is attributed to the eastern edge of the Bactrian Kingdoms in Sinkiang, China (Figure 2.5).

Curiously, in this same area of India, lead coinage reappeared with the Danish colonial outpost of Tarangambadi (Tranquebar) (1620-1845 A.D.). This colonial site issued coins in lead up to 1688 and showed a bilingual marking, similar to the Indo-Greek coins 1600 years earlier.

The Greek tradition of coinage also moved to Egypt and Rome. In Egypt a transfer to an internal



currency (non-Alexandrian) occurred about 310 B.C.

under Ptolemy I (Howgego, 1995) (p. 52). In Egypt silver clad coins and even lead coins were often used with the full confidence of the public (Howgego, 1995) (p. 126). Lead was particularly used in Egypt in the 2<sup>nd</sup> and 3<sup>d</sup> centuries A.D. for small change ((Milne, 1939)). The Roman Imperial mint at Alexandria had stopped issuing much currency and local enterprise necessitated the use of lead coins (dixobols and obols).

A different situation prevailed in Rome proper. Roman coinage followed Greek coinage on the Italian peninsula. Greek colonies (Naples, Taranto, Velia, Herclea, Matapontum, Thurii, and Croton (Burnett) on the Italian peninsula struck silver coins into the late 4<sup>th</sup> century B.C. The Roman republic first struck silver coins about 300

B.C. (See Roman Time line J.15). The amount of silver in circulation rose rapidly (Figure 2.6) with expansion of the Republic and then began to decline. In the Empire debasement of coins (often with lead) was a common practice (Figure 2.6) which Pliny (Howgego, 1995) p. 118) attributed as necessary to finance wars and expansion. Counterfeiting of Roman currency often was associated with silver plating of base metals ((Burnett, 1987), p. 162) including lead ((Milne, 1939)). Along with fraud and counterfeiting, the actual silver currency itself was debased. Septimus Severus advised his sons “to enrich the soldiers and despise the rest.” Harl writes “he implemented his axiom by debasing the denarius and raising salaries. Emperors who improved the purity of the denarius found themselves outbid for the loyalties of the army and so they went down in ignominious defeat” (Harl, 1996) (p. 126).

Lead tokens (as opposed to coins) were frequently used in the Roman era. These tokens were often tossed to the crowds during festivals and were



**Figure 2.8.** Boy Bishop lead token. (Author's collection).



**Figure 2.9:** Lead hops tokens from Victorian England. Author's collection.

redeemable for wine, bread, or prostitutes (Figure 2.7). Similar lead tokens are commonly found in England. Lead tokens were specially struck for the December festival of the Boy Bishop (Figure 2.8). This festival, popular in northern Italy and throughout Europe,

involved the selection in December sometime close to the feast of Saint Nicholas, of a boy to serve as bishop. The boy would wear the bishops robes and preside over ecclesiastical functions with the exception of mass. In Norfolk and at Bury St. Edmond in Cambridge shire England the boy bishop's rule was marked by the minting of lead tokens, known as the Boy Bishops, which were redeemable for a small treat. The practice was abolished by King Henry VIII.

In England lead tokens were minted for the needs of local economies in several distinct periods (Akerman, ; Hume, 1984; Williamson, 1970). The first was during the 16<sup>th</sup> century during the reign of Elizabeth I who demonetized several types of currency in response to the debasement which had been practiced under Henry VIII. The scarcity of small change resulted in the issuance of tokens by shopkeepers. A second time frame was the third quarter of the 17<sup>th</sup> century (ca. 1648-1672). The fall of the monarchy with its monopoly on minting allowed many merchants and municipalities to issue tokens of a variety of metals, including lead. Lead tokens again became common between 1787-1796 and between 1810-1814 (the time frame of the Napoleonic Wars).

These tokens originally arose because the need for small change could not be accommodated by royal manufacture of appropriate intrinsic value pieces of silver. That is, the necessary coins would have been of such a small size and weight of silver that they were easily lost. In response local shopkeepers minted their own redeemable tokens.

Lead tokens for marking of agricultural work were commonly issued in rural England (Norfolk, Cambridge, Nottingham) in the 16<sup>th</sup> and 17<sup>th</sup> century (Figure 2.9). Tokens were also struck by individual farmers in the late 19<sup>th</sup> century and used to mark the number of bushels of hops harvested by farm workers.

As the Empire split into East and West lead coin issue was occasionally found in the Byzantine world. Lead was used for Alexios I's first tetartera. Despite the minor occurrences of lead as true money most coinage was either silver or gold. The largest amount of lead pollution occurred with the advent of the silver coinage of the Greeks and increased with the silver output of the Romans.

Lead tokens as a form of quasi-official currency also show up in the United States. Penny tokens of lead were minted by various local groups during the Civil War (Figure 2.10). Counterfeiting by silver plating of base metal (as noted during the Roman



**Figure 2.10.** A “penny” of lead issued by a grocer during the American Civil war, 1863. Author’s collection.



**Figure 2.11.** U.S. currency counterfeit coin, lead based.

Empire) has also been common, particularly during economic downturns. In 1932 one Marvin Grogg of W. Virginia was arrested in Lawrence County, Ohio for passing fake ½ dollar pieces made of lead which were polished to look like tarnished silver ½ dollars (Ironton Tribune, 17 April, 1932, Man Confesses He Manufactured Lead Coins Here). Figure 2.11 is an example of a counterfeit ½ dollar coin.

Coinage in China developed independently (Price, 1980) from use of shells, bronze tools etc., in 1100 B.C. The first metallic coins of bronze date from about 500 B.C. and were shaped like various

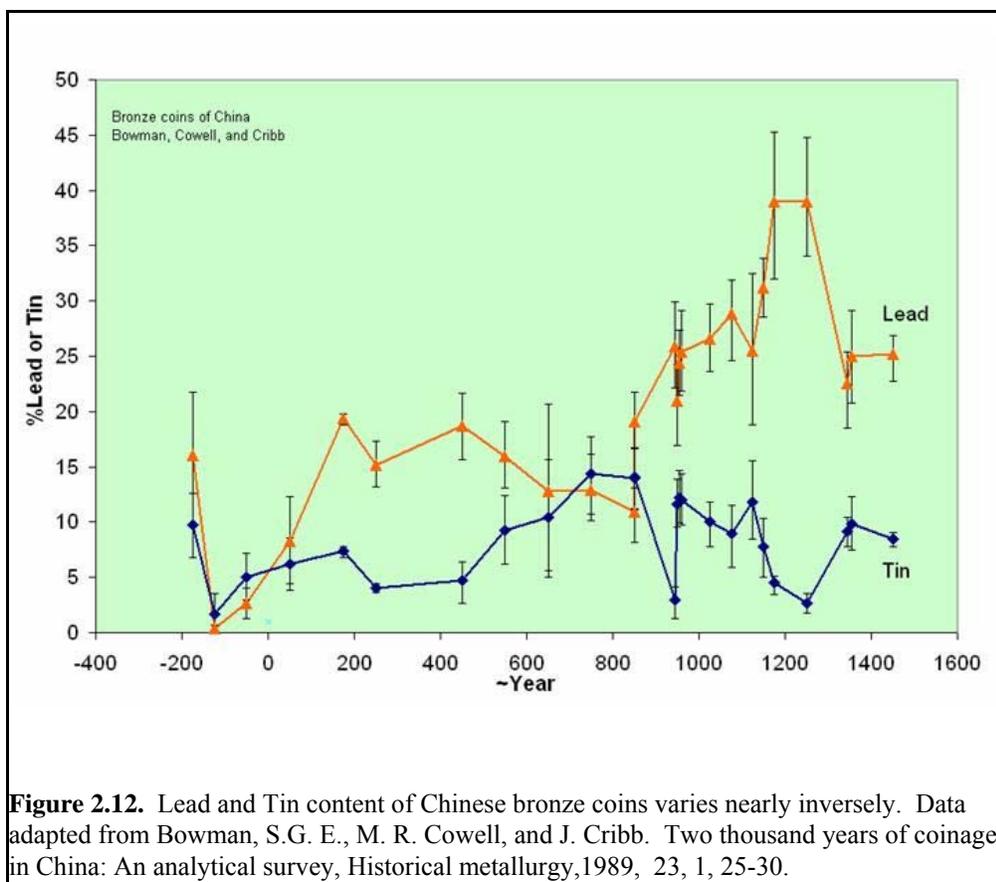
agricultural implements (Gernet, 1968) in the Ch’u kingdom. A chemical analysis of Chinese coinage from the Zhou dynasty (~3<sup>rd</sup> century B.C.) forward indicates that coins were heavily leaded with the lead content increasing with time. Brass coins introduced 1503 to 1505 A.D. were most likely produced with recycled metal as inferred from their heavy lead content (Bowman et al., 1989).

### Cupellation

With the advent of coinage in the West silver production and its associated lead dispersion spiked (Figure 1.3). The reasons for this are two fold. As noted previously, lead is often found in conjunction with silver. A typical reduced silver ore is argentite ( $\text{Ag}_2\text{S}$ , *argen* is Latin for silver, hence the name “Argentina.”) In an ore body the weight to weight ratio of lead to silver is may exceed 400 or 450 to 1 (71 ounces Ag/ton Pb). Around approximately 3000 B.C., the art of cupellation was used to purify silver from lead.

Processing a silver sulfide ore requires some means to purify of the solid metal melt obtained. Lead’s crucial role in this purification process is partly responsible for its unique image in alchemy. The process of using lead in silver purification dates back about 3000 B.C. It appears in important literary illusions:

*The bellows are burned, the lead consumed of the fire;*



**Figure 2.12.** Lead and Tin content of Chinese bronze coins varies nearly inversely. Data adapted from Bowman, S.G. E., M. R. Cowell, and J. Cribb. Two thousand years of coinage in China: An analytical survey, *Historical metallurgy*, 1989, 23, 1, 25-30.

*The founder melteth in vain; for the wicked are not plucked away.*

*Reprobate silver shall men call them  
Because the Lord hath rejected them.*

*Jeremiah 5: 29-30 (610 B.C.)*

*The house of Israel is to me but a dross; all they are brass, and tin,  
And iron, and lead in the midst of the furnace; they are even the dross of silver.*

*Ezekiel 27:12 (~588 B.C.)*

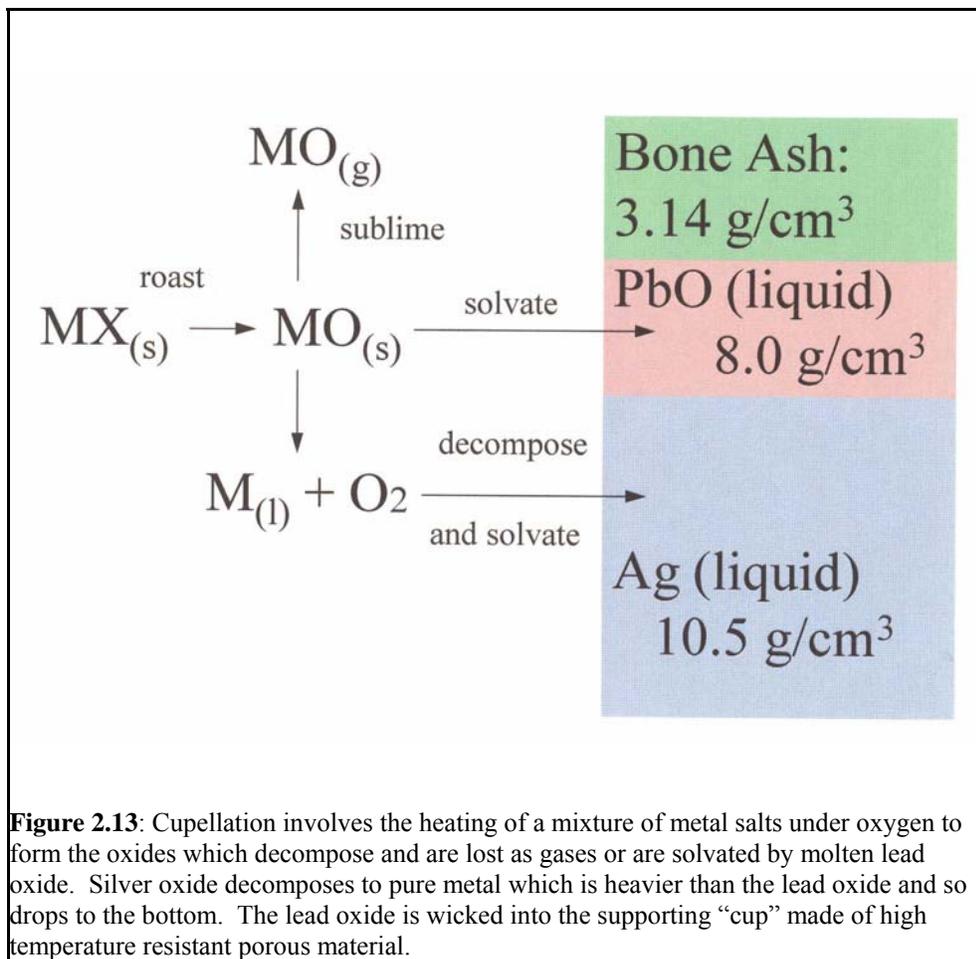
How does cupellation work? It is actually an example of very elegant analytical chemistry involving sublimation, decomposition, solvation, and separation of immiscible liquids by a wicking process.

The generic process begins by forming a “cupel” or cup made of bone ash (Figure 2.14). The ground-up and ashed bones consist of predominately tribasic calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) which does not melt until temperatures 1670 °C. (We noted the stability

of these compounds to high temperatures in Chapter 1 with respect to the formation of planets.)

The accounts of cupellation given by Theophilus carefully specifies extended grinding of this material. The particle size is important because it is desirable to create a fine capillary network of pores. The oxygen content of the ash allows the liquid lead oxide to adsorb to the surface of the capillaries. The  $\text{PbO}$  is thus “wicked” into the ash. Bone ash apparently was not in general use before the Middle Ages (Craddock, 1995), p. 228-9.

Next a mixture of solid metal compounds are added to the cupel, covered with lead and more bone ash (Figure 2.13). The mixture is “roasted” by a flow of hot  $\text{O}_2$ -containing air to form metal oxides. The silver oxide decomposes at 230 °C directly to a liquid to form a liquid silver whose density is 10.5  $\text{g}/\text{cm}^3$ . The solid lead oxide ( $\text{PbO}$ ) present in the original ore, or deliberately added during the cupellation process, melts at 886 °C. This liquid has a density of 8.0  $\text{g}/\text{cm}^3$  and thus will “float” on top of the liquid silver. The metal oxides which do not decompose are partitioned



into the lead oxide liquid which is floating on top of the silver. These combine with the bone ash and are wicked into the “cupel”. This ash has a density of  $5.606 \text{ g/cm}^3$  and thus floats on top of the liquid PbO which itself floats on top of the liquid silver (see Table 2.2 and Figure 2.13).

How does this separation of lead from silver help to refine the silver that contains other impurities? Table 2.2 shows the temperatures of decomposition, melting, and sublimation for various roasted metals (metal oxides). Note that all metal oxides besides silver melt at higher temperatures. Thus, if the cupellation process is kept near  $886\text{-}900 \text{ }^\circ\text{C}$ , unlike the smelting process at much higher temperatures, these metal impurities, because they have been ground, will become soluble in material of like nature. In other words, they will be more soluble in liquid lead oxide than in pure metallic silver. The lead oxide carries the other metal oxide solid impurities into the ash material,

which then rises as a scum that is collected from the surface.

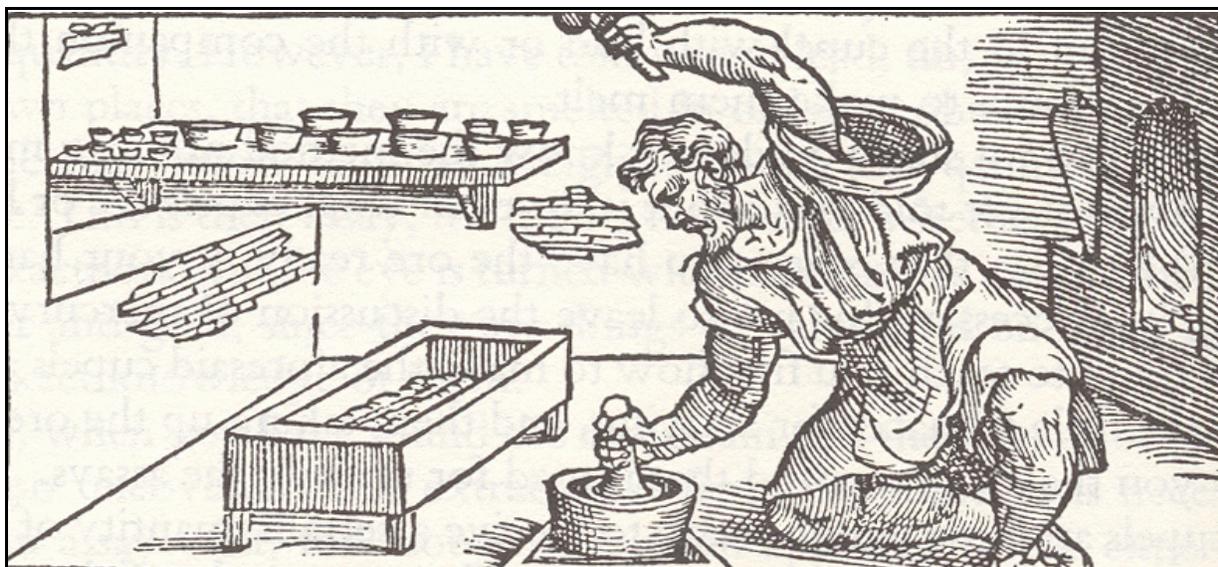
The recovered scum is primarily litharge, lead oxide, PbO, containing a variety of concentrated metal impurities (Table E.8 (Craddock, 1995)).

This purification process does not work for some metals. Tin oxide decomposes near the temperature of cupellation and forms a liquid melt with silver. If glass is added it can ionize, thus changing the ionic composition of the PbO and increasing the solubility of SnO in the PbO before decomposition occurs. (See Chapter 4 for lead and glass). Gold also cannot be removed from silver by this process. Gold oxide decomposes at  $-0.16 \text{ }^\circ\text{C}$ , forming liquid gold, which is soluble in the liquid silver. ZnO, while stable, is insoluble in lead oxide.

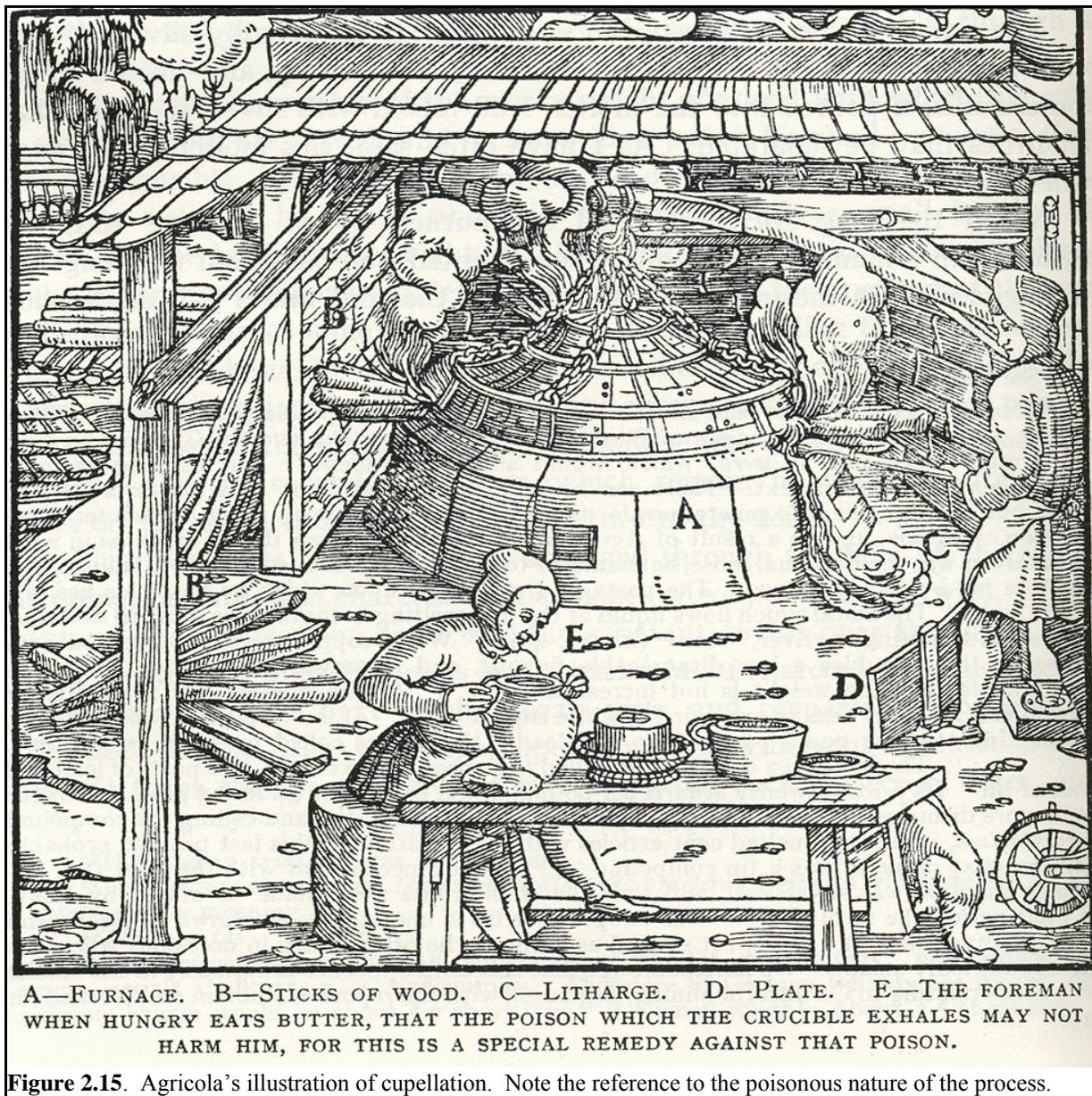
This purification process has continued in an unbroken fashion to modern times. The process is used

**Table 2.2: Chemical Properties Relevant to Cupellation**

| <u>Metal Oxide</u><br><u>Metal</u> | <u>Data Relevant to the Metal Oxide</u> |           |           |                         | <u>Data Relevant to the Pure</u> |                |                         |
|------------------------------------|---|-----------|-----------|-------------------------|----------------------------------|----------------|-------------------------|
|                                    | Decomposes                              | Sublimes  | Melts     | Density                 |                                  | Melts          | Density                 |
|                                    | <u>°C</u>                               | <u>°C</u> | <u>°C</u> | <u>g/cm<sup>3</sup></u> | <u>Metal</u>                     | <u>°C</u>      | <u>g/cm<sup>3</sup></u> |
| Au <sub>2</sub> O <sub>3</sub>     | -0.160                                  |           |           |                         | Au                               | 1064.43<br>(l) | 19.3                    |
| Ag <sub>2</sub> O                  | 230                                     |           |           |                         | Ag                               | 931.93         | 10.5                    |
| As <sub>2</sub> O <sub>3</sub>     |   | 193       | 312       | 3.43                    |                                  |                |                         |
| Sb <sub>2</sub> O <sub>3</sub>     |   |           | 656       | 5.67                    | Sb                               | 630.74         | 6.684                   |
| PbO                                |   |           | 886       | 8.0                     | Pb                               | 327.1          | 10.686                  |
| SnO                                | 1080                                    |           |           |                         | Sn                               | 231.8          | 5.75/7.28*              |
| CuO                                |   |           |           | 1235                    |                                  |                | 6.0                     |
| Cu <sub>2</sub> O                  |   |           |           | 1235                    |                                  |                | 6.0                     |



**Figure 2.14.** Biringuccio's (1540) image of striking cupels from a paste of ash (in rectangular box). Cupels formed and drying in upper left corner. Biringuccio's *Pirotechnia*, ed. Smith and Gnudi, Dover, N.Y., 1990, p. 138.



by silver workers in India. The exposure of these workers to the fumes of lead oxide has led to acute clinical saturnism (abdominal colic, weakness, constipation, and motor neuropathology) (Tandon et al., 2001).

Figure 2.15 shows an example of 1500s European cupellation from Agricola. Note the reference to lead poisoning in the Figure. Figure 2.16 shows an image of Aztec metallurgy in which oxygen is blown into a carbon covered fire (Miller and Taube, 1993).

### Descriptions of Cupellation

A description of cupellation is given by Roger of Helmarshausen (“Theophilus”) in his “On Divers Arts” (~1100 A.D.) (Hawthorne and S., 1963). His clear description may be explained by the fact that he, himself, was a superb metallurgist.

*Chapter 23, Book III. Refining Silver*



**Figure 2.16** Aztec metallurgy from the Florentine Codex, Book 9, 1500s.

*Sift some ashes, mix them with water and take a fire-tested earthenware dish of such a size that you believe the silver which is to be refined can be melted in it without running over. Put ashes in it, thinly in the middle and thickly around the rim, and dry it in front of the fire. When it is dry, remove the coals a little distance from the [wall of the] forge and put the dish*

*with its ashes in front of the wall beneath the tyuere [hole], so that the blast from the bellows will blow onto*

*it. Then replace the coals on top, and blow until the dish is red-hot. Then put the silver into it, add a little lead on top, heap charcoal over it, and melt it. You should have at hand a stick cut from a hedge and dried in the wind, with which you should carefully uncover*

*the silver and clean away whatever impurity you see on it. Then put on it a brand, that is, a stick burnt in the fire, and blow gently, using a long stroke [of the bellows]. When you have removed the lead by this blowing, if you see that the silver is not yet pure, again add lead, place charcoal on it, and do as you did before. However, if you see the silver boiling and jumping out, know that tin or brass is mixed with it, and finely crush a small piece of glass and throw it on the silver. Then add lead, put charcoal on, and blow vigorously. Then inspect it as before, take away the impurities of glass and lead with the stick, put the brand on it, and do as before. Keep on doing this until it is pure.*

*Chapter 69: How to Separate Gold From Copper*  
*Now if you ever break gilded copper or silver vessel or any other kind of gilded work, you can recover the gold in this way. Take the bones of any kind of animal that you may have found in the street and burn them; when they are cold, grind them very fine and mix with them a third part of beechwood ashes and makes dishes, as we described above in the refining of silver. Dry these by the fire or in the sun. Then carefully scrape the gold off the copper and wrap the scrapings in lead that has been hammered flat and thin. Set one of these dishes into live coals on the forge, put the lead packet with the scrapings into the dish as soon as it is red-hot, heap charcoal over it and blow. When it has melted, burn it in the same way that silver is normally refined, sometimes removing the live coals and adding lead and sometimes uncovering it and blowing carefully, until the copper is completely consumed and pure gold appears.*

A more garbled account (copied by medieval monks from earlier recipes, dating to about 900 A.D.) is given in the *Mappae Clavicula*.

*Recipe 84: How black silver should be made white*

*Take 2 solidi of miniu (cinnabar) from which quicksilver is made, which is washed in hot water and when dried, is ready for use. Melt it, and mix in a little bit of copper with silver and lead. Now, all of these accept lead [when] they are melted, and so a more resplendent sign is achieved.*

The *Mappae Clavicula* recipe is difficult to interpret, with the exception of the comment that all of the metals “accept” lead. A better recipe was given some 400 years later by George Bauer better known as Agricola (1490-1555 A.D.).

*Take horse bones burned and pulverized, and wood*

*ashes, well washed with an equal part of the bone ash, moisten these and strike cupels which are good. On the newly made cupels sift through a very fine sieve on the deepest part bone ashes from calf's head or fish bone or pike's head to thickness of a poppy leaf, and then give it a blow with the stamp. This gives good cupels. Let them dry well and the older such cupels are the better they become. Sprinkle burned and powdered pike bone on the cupels when you wish to test an ore.*

Abul Fazl's *Ain-I-Akbari*, a medieval Indian text describes cupellation in some detail. *They dig a hole, and having sprinkled into it a small quantity of wild cow dung, they fill it with the ashes of mughilan wood, then they moisten it, and work it up into the shape of a dish, into this they put the adulterated silver, together with a proportionate quantity of lead. First, they put a fourth part of the lead on the top of the silver and having surrounded the whole with coals, blow the fire with bellows, till the metals are melted. Which operation is generally repeated four times. ...* (Sayed, 1988), p. 101.

## LEAD AND SILVER MINING

We will examine in some detail several ancient lead and silver mines that achieved worldwide fame: the lead/silver mine of Laurion in Greece, the Roman silver mine of Rio Tinto, Spain, the German mines, and various New World operations. Important in the functioning of each mine was the silver content per lead ore, the source of lead if the silver was found independently of lead, the source of fuel, and the source of labor. Each mine helped to shape political events.

## Fuel in General: Efficiency of Wood

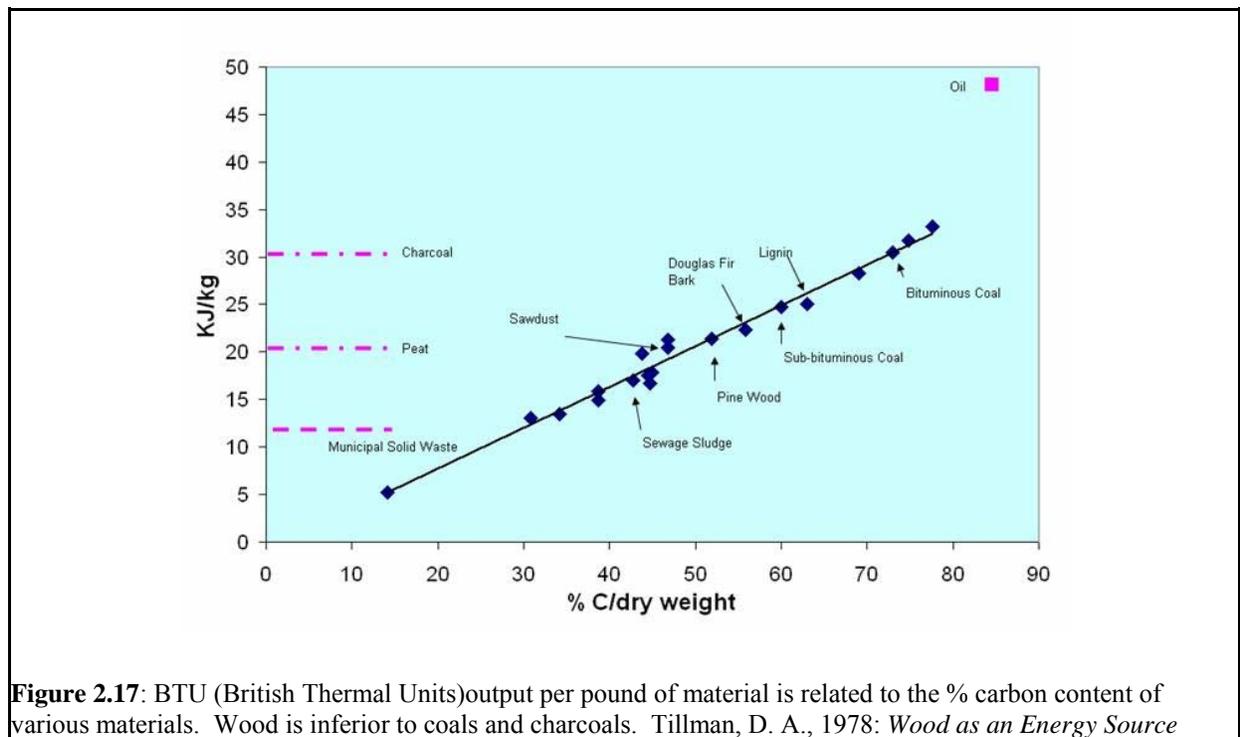
Full exploitation of mines required energy (often human) for extraction and for the cupellation process. The only source of fuel in early mining was wood. Wood's fuel efficiency depends primarily upon its moisture content and density (Figure 2.17 (Tillman, 1978), p. 70-75). (Table C.5 shows the bulk composition of various woods and their energy outputs BTU (British Thermal Units = 110154.35 J, or the energy required to raise 1 pound of water 1°F). The figures show a direct correlation between the amount of energy produced and the carbon content of the fuel. The total energy output of wood is not as high as that of materials higher in carbon, such as charcoal or coal.

Charcoal can easily be made by slowly burning soil-covered hardwood in a kiln. A typical medieval European collier (charcoal maker) cut wood into 4 feet lengths and stacked it on a "pitcher's mound," which had a diameter of about 40 feet. On the center of the mound, a type of chimney was constructed from larger pieces of wood. The chimney was filled with smaller pieces and then surrounded by more wood. The whole mound of wood was covered with leaves and 1 to 3 inches of soil in order to prevent a full-fledged fire from turning wood to ash instead of

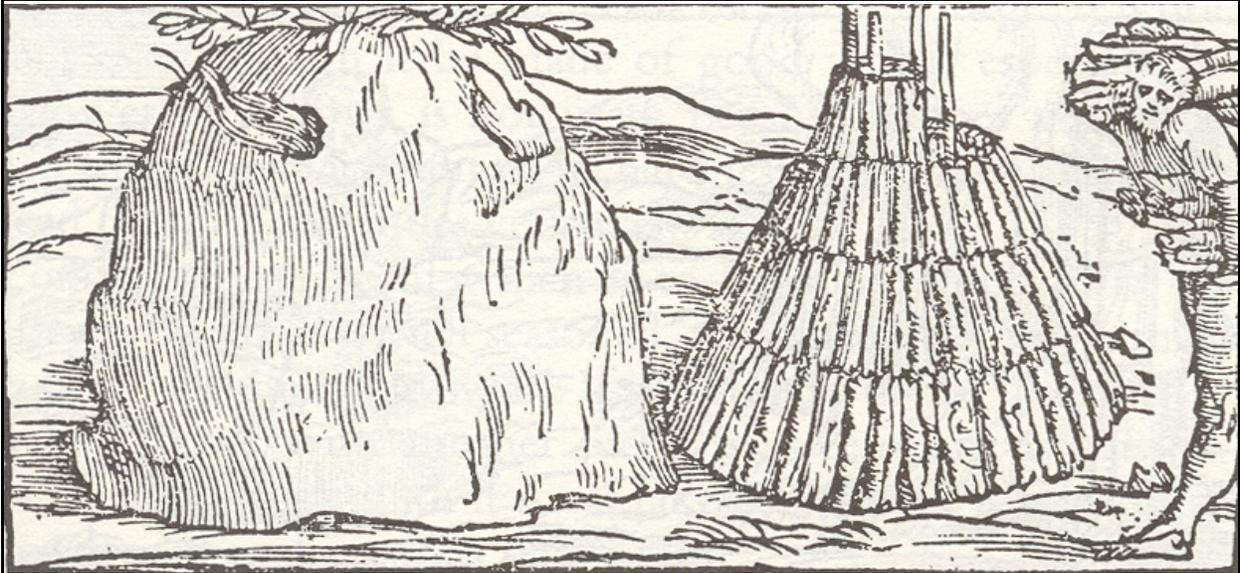
coal (Figures 2.18 to 2.21). The burn took 3-10 days (Crumrine, 1994).

Charcoal gives a specific energy, or energy per unit weight, of 28.33 MJ/kg, comparable to that of coal (25-35 MJ/kg). Because its specific heat is high compared to that of wood (16-21 MJ/kg), it is still a desirable form of energy and constitutes a significant portion of energy consumption in Africa in the late 1900s. Figures 2.20 and 2.21 illustrate contemporary charcoal production in Africa.

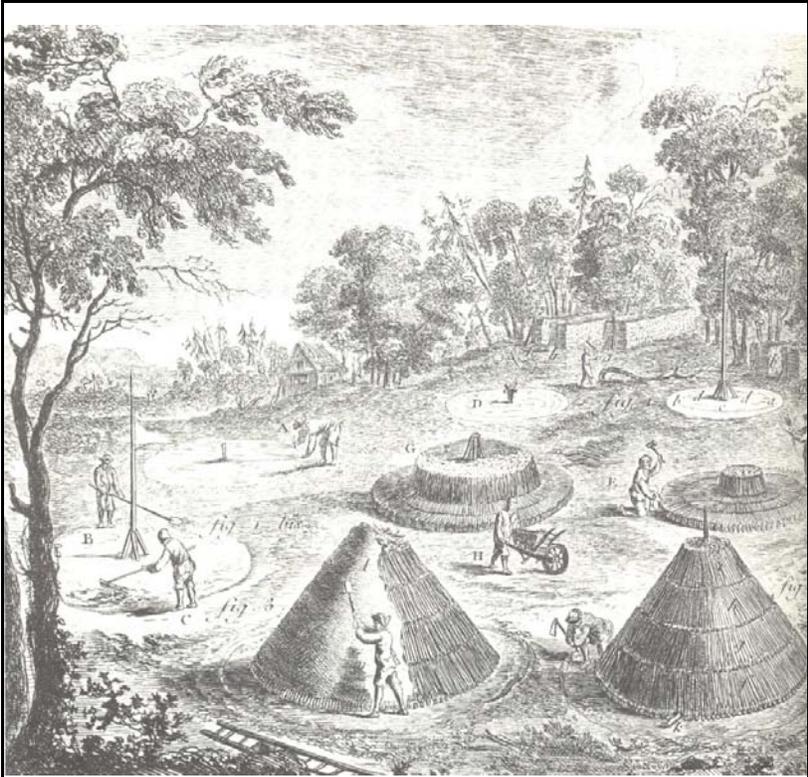
Because wood was necessary for silver mine output control of wood supplies was an important part of the social equation in mining.



**Figure 2.17:** BTU (British Thermal Units) output per pound of material is related to the % carbon content of various materials. Wood is inferior to coals and charcoals. Tillman, D. A., 1978: *Wood as an Energy Source*



**Figure 2.18.** Biringuccio's (1540) image of staking wood to create charcoal. Biringuccio's *Pirotechnia*, ed. Smith and Gnudi, Dover, N.Y., 1990, p. 177.



**Figure 2.19** Engraving of charcoal production , *A Forest Journey*, John Perlin, 1989



**Figure 2.20** Soil-covered wood stack in Africa burning to charcoal and smoking. Source: Stockholm Environmental Institute, Chaposá Program.. [http://www.sei.se/chaposá/photogallery\\_chproduction.html](http://www.sei.se/chaposá/photogallery_chproduction.html). Nov. 4, 2002



**Figure 2.21** Final charcoal stack after soil removal. Source: Stockholm Environmental Institute, Chaposá Program. See Figure 2.20 for source.



**Figure 2.22.** Aegean Ore Deposits. Squares are lead ores, colored squares gold ores. Solid black triangles designate ancient lead mines and open black triangles evidence of processing activity such as slag heaps and litharge. If the solid triangle surrounds a colored dot, it indicates modern mining. Noel H. Gale and Zofia Stos-Gale. Lead and Silver in the Ancient Aegean in *Scientific American*, 1981. 244 (6), 176-192.

## Greece

As discussed in the sections entitled “Coinage” and “Cupellation” global lead dispersion began with the advent of Western silver coinage. Silver coins came into widespread use among the Greeks between 700 and 500 B.C. The source of the silver has been extensively investigated. There were three main sources of silver in Greece: Siphnos which had a maximum productivity in the 7<sup>th</sup> and 6<sup>th</sup> centuries B.C., Paeonia, and Laurium between the 6<sup>th</sup> and 3<sup>rd</sup> centuries B.C. (Milne, 1939).

Lead deposits in the Aegean are shown in Figure 2.22. Important mines were established on the Islands of Siphnos, Samos, Euboea, and Lesbos, as well as in the Chalcidike mountain region of Thrace (Treister, 1996), p. 23. Many of the Greek islands were actively mined, although they were depleted by about 500 B.C. The Siphnos silver mine was exhausted 516 B.C. according to the writer Pausanias X.8 XI.2.

The best known and most studied Greek mine was that of Laurion or Lavrion (Figure 2.22). The mines were in use, as determined by Minoan lead isotope measurements consistent with the Laurion mine, during Mycenaean times (2000-1500 B.C.) (Shepherd, 1993), p. 75. Lead from Laurion has been found in Egyptian bronzes dating to 767 B.C. (Fleming, 1982). The Laurion sites may have been more intensively exploited after the loss of Macedonian and Thracian mines to the Persians in 512 B.C.

The silver mines contributed to the wealth of the city of Athens as early as 510 B.C. Their products inspired the initiation of Athenian coinage. The value of early, primitive coinage often was based on total weight, and not upon the noble metal (i.e., gold, silver, or copper) content. As a consequence highly leaded coins were produced to increase weight in the initial phase of coinage, as was the case for Etruscan and Umbrian coins of 400 B.C. where the lead content ranged from 20-60% (Craddock and Burnets, 1998). Early Chinese coinage used a similar high lead



**Figure 2.23.** Depiction of mining during Grecian times, 550 B.C. National Museum of Athens. In Healy: *Mining and Metallurgy in the Greek and Roman World*, 1978, plate 8.

preceding the use of true gold, silver, or copper coinage (Zhiqiang and Weirong, 1998). The primitive coinage was followed by coinage in silver and gold.

Greek silver coins made with Laurion lead and dating to 580 B.C. were produced in Corinth and Aegina (Tylecote, 1976), p. 50. These coins give a record of the mine's ore content. Silver coins from 500-300 B.C. contain 93-99% silver. Those from 186-169 B.C. contained ~95% silver with 0.0076-0.33% Au and 0.035-5.3% Cu. The presence of gold indicates that no attempt was made at that time to chemically separate it out. Table E.1 shows the composition of early coinage from that time period (Elam, 1931; Hill, 1922; Tylecote, 1976), p. 51.

The composition of the ore was on the average 65% lead (Davies, 1979). The ore is estimated to have contained 2176 g Ag/ton (Tylecote, 1976). Conophagos estimates that the ancient Laurion mine's average ore was 50% by weight lead. Of the 87.4% of the lead recovered, 94.8% of the silver was also

recovered.

An estimate of the amount of lead produced from the mine is 1 million tons (Davies, 1979), p. 251.

The history of the mine's use is closely related to the political history of Athens. The expansion of Athenian power began in 482 B.C. under Themistocles, who built a fleet of ships requiring either wood from Mount Ida or from Macedonia. The Athenian fleet successfully

defeated Persia in 480 B.C., a time coinciding with the opening of a rich vein of galena/silver at Laurion (Forrest, 1986), as described by Herodotus (VII.144). Some estimate that 20 tons silver/year were produced during this time period. The smelting of this ore along with the construction of Athens and the fleet, resulted in depletion of local wood sources. Prior to the operation of the Laurion mines, pines grew freely on the peninsula of Sounion (Meiggs, 1982), p. 203. The countryside near Athens was well wooded up to 6th century B.C. (Perlin, 1989), p82, as shown by Plato's statement that neighboring timber was used for house construction in the city of Athens. This local supply of wood was used to build the ships that defeated the Persian invasion of Xerxes.

With the depletion of local wood supplies the Athenians needed to find alternative sources. In 465 B.C. the Athenians sent 10,000 colonists to Amphipolis to secure this wooded region near Philippi (see map, Figure 2.22).

The growth of Athens was not unnoticed by

Sparta its neighbor on the Peloponnesian peninsula. Athenian expansion fueled the Peloponnesian War (431-421 B.C.). It was during this time, that of Pericles, that the silver mines at Laurion reached their maximum production.

Pericles (490-429 B.C.), the leader of the Athenian democratic party, ruled during the Peloponnesian War) (Conophagos, 1982). In the first phase of the war, Amphipolis was lost. Athens itself was occupied and the last of its forests destroyed. This phase of the war closed with the peace of Nicias. Athens reinitiated the war with an attempt to secure the island of Sicily and its woods in 415 B.C. In doing so Athens lost its fleet. A new fleet, built with wood from Macedonia, proved futile in the end, as the Spartans obtained wood for their fleet from their Persian ally, Pharnabazus.

By the end of the Peloponnesian War (404 B.C.), wood was so scarce that the smelting operation at Laurion was moved to the coast, where imported fuel could be obtained (Perlin, 1989), 95. The coastal towns involved in smelting were Panormou, Thorikos, Megala, and Pevka. These coastal operations used less charcoal and thus generated less waste lead, although silver did remain in the furnace. The reduction in use of fuel allowed the mines to help revive the Athenian economy after the Peloponnesian War. 340 B.C. marked a high point in production, with 140 mines leased from the state for periods of 3-7 years. 26.2 tons of silver and 8.7 tons of lead were produced per year (Treister, 1996), p. 183. Even with the reduction in wood use, silver smelting at Laurion used more than 24 million pines or 52 million oaks. Most of this wood was imported from Macedonia and that led to that nation's political rise. "We import timber with great trouble from distant parts, in Macedonia there is a very cheap supply" (*Demosthenes*). Demosthenes accused Meidias of privately using a ship to bring wood to his silver mines.

In 370 B. C. Athens sent Iphicrates and his army to recover Amphipolis. In the process, Philip of Macedonia, the father of Alexander, was able to obtain control of the timber lands by 356 B.C. This event marked the end of Athenian influence in the area. The Chalcidian League of northern Greek cities also relied upon Macedonian wood. In order to weaken the Chalcidian League Sparta sent 10,000 troops to oust the League from Macedonia.

Ownership of the leases affected party politics. Silver flooded the world market after Philip II of Macedonia captured the Thracian mines. Silver prices dropped giving lease holders a reason to oppose

the Macedonians. The decay of Athens is documented in its inability to extract enough silver to pay for the removal of Macedonian troops in 229 B. C. Labor unrest also contributed to the demise of the mines. A slave revolt in the second half of the 2nd century B.C. resulted in the capture of the Acropolis at Sunion and the devastation of Attica (Poseidonius in Athenaeus VI.272). Strabo (IX.1.23) indicates that in his time (~100B.C.) the mines were exhausted.

Labor was an important component in exploitation of the mines. Xenophon, (an Athenian general who lead 10,000 Greeks into Asia Minor in 400 B.C. mentions the mines at Laurion several times, in connection with lease holder Nicias. He refers in *Memorabilia* (Book II, Chapter 5) to Nicias during a Socratic discourse. Socrates is supposed to have said,

*"Anthisthenes," he said, "are friends worth certain amounts just as household servants are? For I suppose among household servants, one is worth two mina, another not even a half-mina, another five mina, and another even ten. And Nicias the son of Niceratus is said to have purchased an overseer for his silver mines at the cost of a talent. I am examining this," he said, "whether, just as household servants, so friends too have worth."*

An Athenian man received a three-obol daily stipend for jury duty. One mina was equal to 600 obols. A talant was worth 60 mina, or 36,000 obols (Bonnette, 1994), p. 52.

Nicias was a well-known a general of the Athenians wars with Sicily. His biography appeared in Plutarch's Lives) (Perrin, 1916). Nicias made his wealth by contracting slave labor for the silver mines (*Nicias, IV.*):

*...it is recorded that [Nicias] sacrificed every day to the gods, and that he kept a diviner at his house, ostensibly for the constant enquiries which he made about public affairs, whereas most of his enquiries were really made about his own private matters, and especially about his silver mines; for he had large interests in the mining district of Laurium, and they were exceedingly profitable, although worked at great risks. He maintained a multitude of slaves in these mines, and the most of his substance was in silver.*

In his comparison between the lives of Nicias and Crassus, Plutarch writes:

*I. In comparing the men, first, the wealth of Nicias was acquired in a more blameless manner than that of Crassus. For although it is true that the working of mines cannot be highly regarded, since most of it is carried on by employing malefactors or Barbarians, some of whom are kept in chains and done to death in damp and unwholesome places, still, when compared with the public confiscations of Sulla and the making of contracts where fire is raging, it will appear in the more favorable light. For Crassus openly utilized these opportunities as men do agriculture and money-lending.*

Vast numbers of slaves were used in the mines. Xenophon, in his *A Discourse upon Improving the Revenue of the State of Athens* (Ashley Cooper et al., 1832), p. 681, gives due consideration to the labor requirements for working the mines:

*IV. Our silver mines alone, if rightly managed, besides all the other branches of our revenue, would be an inestimable treasure to the public. But for the benefit of those who are unskilled in inquiries of this nature, I design to premise some general considerations upon the true state and value of our silver-mines, that the public, upon a right information, may proceed to the taking such measures and counsels, as may improve to the best advantage.*

*No one ever pretended from tradition, or from earliest accounts of time, to determine when these mines first began to be wrought, which is a proof of their antiquity; and, yet as ancient as they are, the heaps of rubbish which have been dug out of them, and lie above ground, bear no proportion with the vast quantities which still remain below, nor does there appear any sensible decay, or diminution in our mines; but as we dig on, we still discover fresh veins of silver-ore in all parts, and when we had most laborers at work in the mines, we found that we had still business for more hands than were employed.*

*Nor do I find that the adventurers in the mines retrench the number of their workmen, but purchase as many new slaves as they can get; for their gains are greater, or less, in proportion to the number of hands they employ...*

He thus proves that the mines will continue to yield:

*It is very strange, that after so many precedents of*

*private citizens of Athens, who have made their fortunes by the mines, the public should never think of following their example: for we have heard, that Nicias, the son of Niceratus, had a thousand slaves employed in the mines, whom he let out to Sosias the Thracian, upon the condition to receive an obolus a day, clear of all charges, for every head, and that the same complement of workmen should be always kept on foot.*

*In like manner Hipponicus had 600 slaves let out at the same rate, which yielded him a revenue of a mina a day, and Philemonides 300, which brought him in half a mina a day, and many others made the same advantage, in proportion to the number of slaves they possessed...*

*In the proposals which I offer, there is only one thing new, namely, that as private men have a constant revenue coming in from the slaves whom they let out to work in the mines; so the public, in imitation of their example, should purchase as many slaves to be employed in the same manner....It is plain that the state can bear the charge of the price of the slaves better than private men; and nothing can be easier than for the senate to make proclamation for all that have slaves to sell, to bring them in, and then buy them up for the public use....*

*And that the public may be no loser by the desertion of slaves, or other accidents, the adventurers in the mines should be obliged to give good security to save the state harmless..... But when our slaves are burned with the public mark of the state, with severe penalties to be inflicted upon all that buy, or sell them; what danger is there of their being stolen?.....*

*Twelve hundred slaves, when bought, will probably in five or six years' time, produce a revenue sufficient to purchase as many more as will make the number 60000. This number, at the rate of an obolus a day a head, clear of all charges, will afford a yearly revenue of sixty talents....*

The mines were not a salubrious work place. The guard niche at the entrance, shafts sized for pre-adolescent labor, and skeletons and evidence of living 300 feet down all suggest this (Murray, 1986). Not all laborers were slaves, as work continued after 20,000 slaves defected in 413 B.C. following the Peloponnesian capture of Deceliea (Shepherd, 1993), p. 74. The defection hurt, however, as the country

began issuing copper coins in 406 B.C.

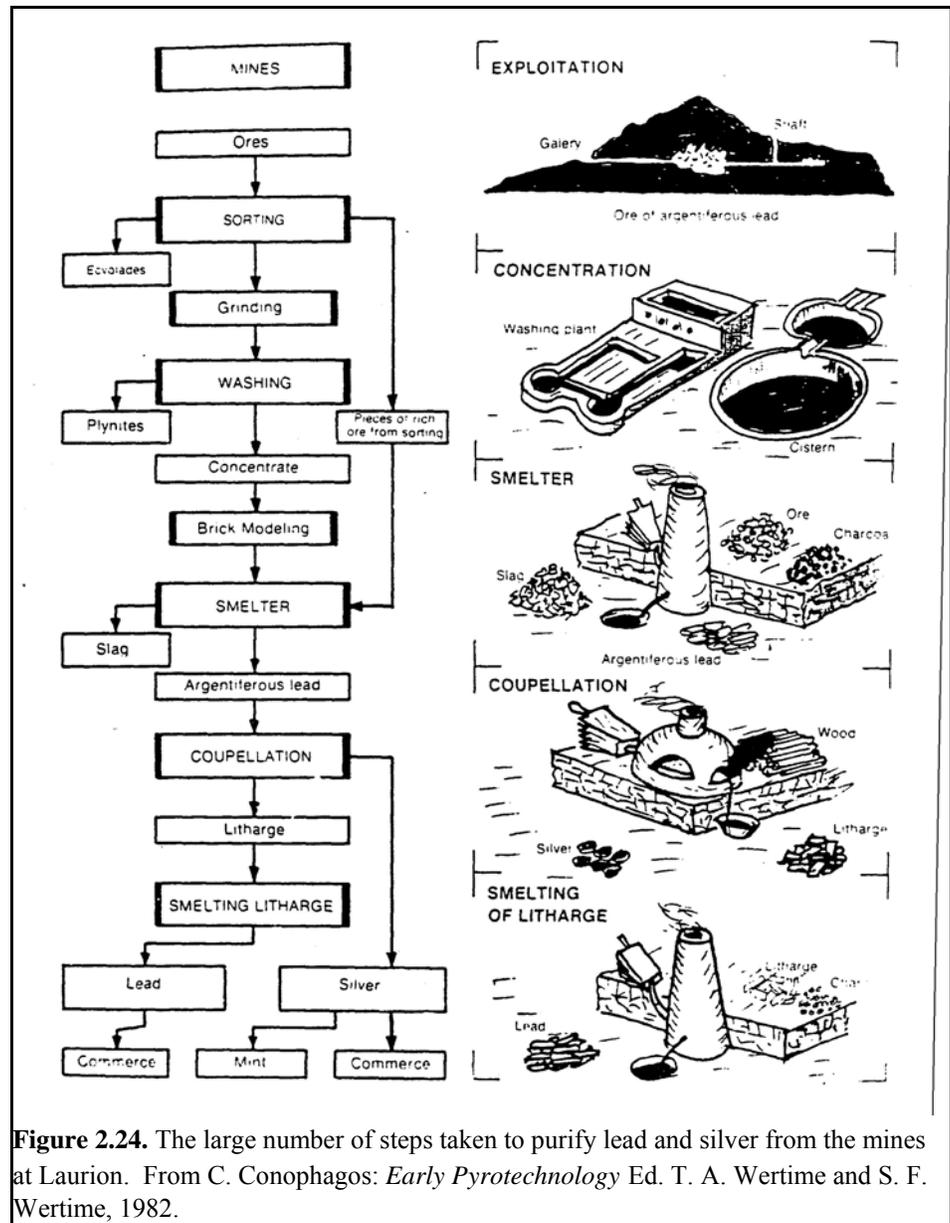
The mine shafts were 111m deep and 1.25 by 1.5 m wide. A good workman could cut a 100 m shaft (12x12 cm) in approximately 3 years (Shepherd, 1993), p.87. The narrowness of the galleries was due in part to a desire to avoid timbering and to follow only the richest vein. No drainage was required. Ventilation, however, was difficult because of the winding side galleries. A miner at rest needs 0.008 m<sup>3</sup> air and 0.02 m<sup>3</sup>/min while working. The size of the shafts would preclude a high air velocity, since the workers filled up most of the shaft (Rosen, 1943), p. 17-19. Possibly 12 to 15% of the workers may have died from oxygen deprivation. Some cross ventilation could be obtained by cross cutting galleries between individually owned shafts. Sometimes fires were placed midway in the shaft to provide an updraft (and down draft elsewhere) to increase ventilation. Fires were lighted at the bottom of shafts to create an upflow of air.

Children were employed as porters because they could fit through the small shafts. Agatharcides *Diordorus Siculus iii, 13, 1*, describes conditions at a Greek run Nubian gold mine:

*The hardest of the auriferous strata they expose to a hot fire, and so loosen its texture, before they proceed to work upon it; but the kind of rock which is less firm, and yields to a comparatively slight force, they break up with quarrying implements, and on this task thousands of these unfortunates are employed; and the strongest in limb of those who are doomed to this hard lot break away the glittering quartz with iron hammers - and that by main force in default of skill - and excavate subterranean*

*passages, not indeed in straight lines, but following the cleavage of the gleaming rock... On this they are unceasingly occupied under the lash of an exacting taskmaster. Then the children who are under age penetrate through the galleries into the chambers hollowed in the rock, and having laboriously thrown up the fallen pieces, convey them into the open to set apart for the purpose outside the pit's mouth. ....*

*Those who are thus condemned to penal servitude, being very numerous, and all in fetters, are kept*



**Figure 2.24.** The large number of steps taken to purify lead and silver from the mines at Laurion. From C. Conophagos: *Early Pyrotechnology* Ed. T. A. Wertime and S. F. Wertime, 1982.

*constantly at work both by day and by night without any repose, and are jealously guarded to prevent their escape; for they are watched by companies of barbarian soldiers who speak a language different from theirs, to prevent their winning any of them over by friendly intercourse or appeals to their humanity....Unkempt, untended as they are, without even a rag to hide their shame, the awful misery of these sufferers is a spectacle to move the hardest heart. None of them, whether sick or maimed or aged, not even weak women, meet with compassion or respite; all are forced by blows to work without intermission, until they expire under this hard treatment. So overpowering is their affliction, that they are ever anticipating worse evils in the future, and welcome death as a blessed change from life. (De Rerum Natura vi, 808ff*

Figure 2.24 shows the complex industrial processing of the ore body at Laurion (Conophagos, 1982). After digging, galena and cerussite were hand sorted. Pieces with low lead content were ground and then sieved under water for concentration of heavier weight lead (i.e., that containing 40 to 50% Pb). The lightweight tailings were settled in a settling basin, and water was recovered. This is not as simple as it sounds. At the time, there was no known way to form cisterns that were large and water-impervious. Such cisterns would have required cement. Cement technology qualifies as a “pyrotechnic”. The Greeks had to construct an impervious barrier with the byproducts of the lead smelting process.

The mortar in the cistern basins at Laurion has been analyzed and reproduced. The formulation of the mortar is as follows. Mix 20-30% litharge (PbO) was mixed with slag or left over ore. This mixture was melted and poured into water to initiate a rapid-forming and fine particle-sized solid. This amorphous glassy material was ground to a fine powder. Lime was added. The resulting plaster was composed of  $\text{PbCO}_3$ ,  $\text{Pb}_4\text{SiO}_6$ , and PbO yellow and red (litharge and massicot). The lead silicate is the component that imparted low porosity and hence water-retaining power (Conophagos, 1982).

## Rajasthan, India

As discussed above in the sections on “Coinage” and “Cupellation” global lead dispersion began with coinage in the western world. Coinage in India appears about the time of the invasion of Alexander. Unlike Greek proper or Rome, official coins were often struck with lead, particularly in S. E. India.

Although there are few lead mines in India (see Chapter 1), a large concentration them can be found in the Aravalli Hills of Rajasthan, India (Figures 2.25 and 2.26). The mines of Dariba and Zawar are of great age. They might have been the source of lead used in the ancient cities of Harappan and Mohenjodaro, although a lead isotope match has not yet been made (Agrawal, 1990),(Bhardway, 1990),(Bhattacharyya, 1988),(Casal and Nindowari, 1966),(Chakrabarti, 1995),(Gordon et al., 1958),(Heine-Geldern, 1956),[Kroeber, 1940

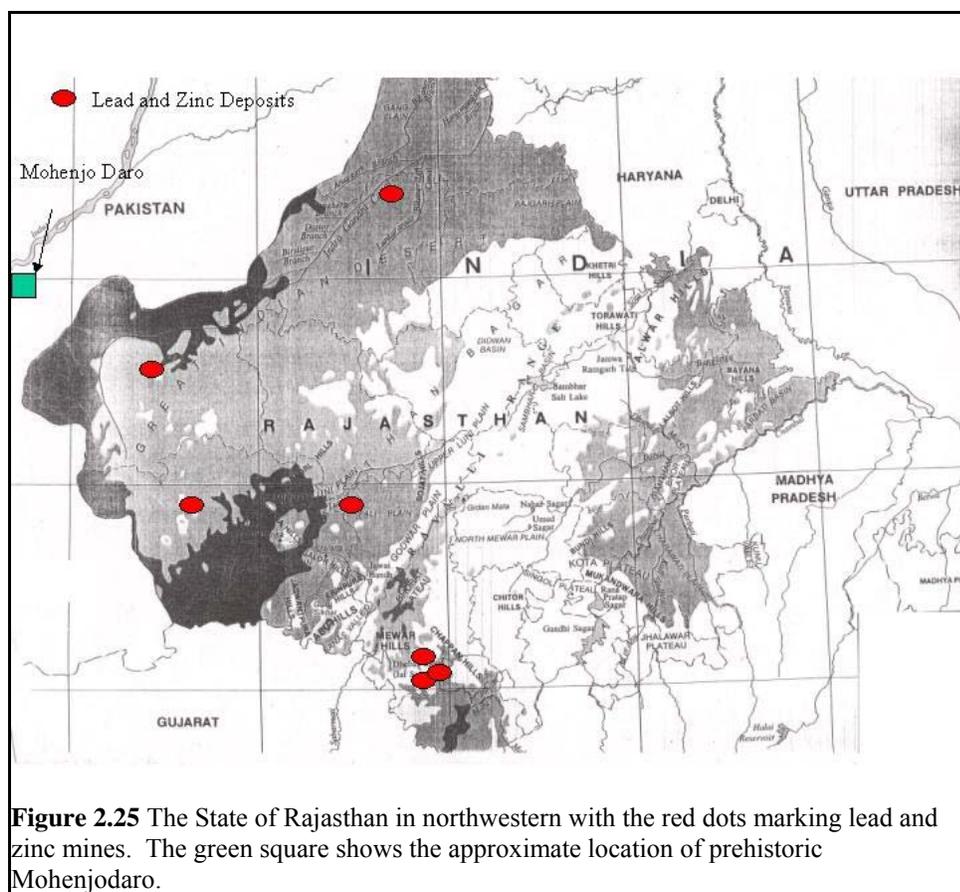
#294],(Lal and Thapar, 1967),(Marshall, 1931),(Nissen, 1988),(Raikes, 1967),(Shaffer, 1992),(Wheelen, 1956).

These cities flourished from 2600-1800 B.C. and abruptly died out shortly before Indo-Europeans arrived in 1500 B.C. It is believed that the civilization of Harappan and Mohenjodaro domesticated cotton and spread cotton technology to Mesopotamia.

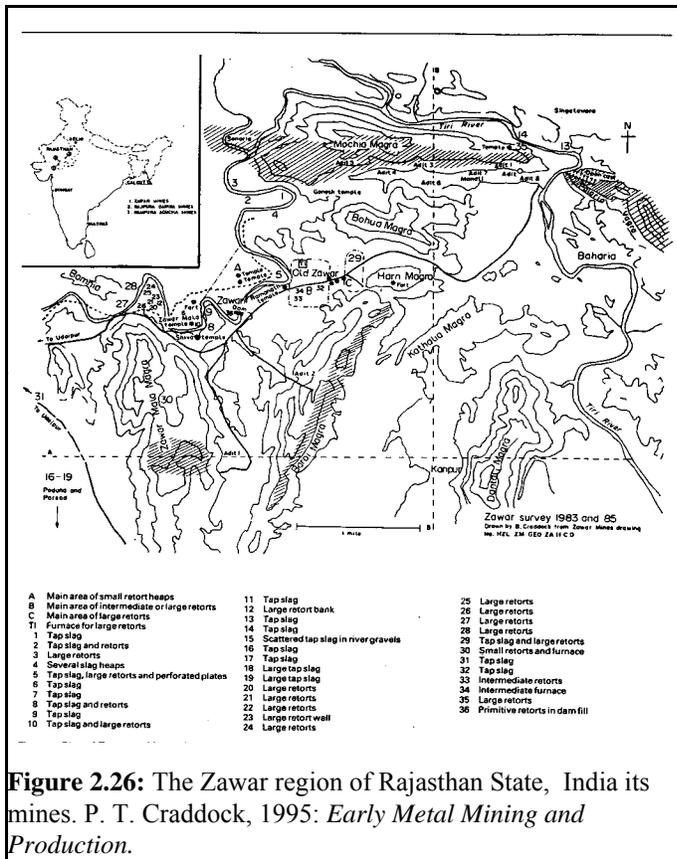
The Aravalli mines were clearly important during the Mauryan transcontinental empire of Ashoka (died 232 B.C.), perhaps because of the first Indian coinage (Craddock, 1995; Willies, 1987).

Geologically, Dariba consists of a flat or weathered plain dotted with erosion resistant silicates (Figure 2.27) (Craddock et al., 1987). The veins run down directly into the plains, meaning that ditches were not efficient at removing water. The main ore body is galena (PbS) with sphalerite (ZnS) and marcasite (FeS<sub>2</sub>). The gossan surface has been oxidized to anglesite (PbSO<sub>4</sub>) and cerussite (PbCO<sub>3</sub>).

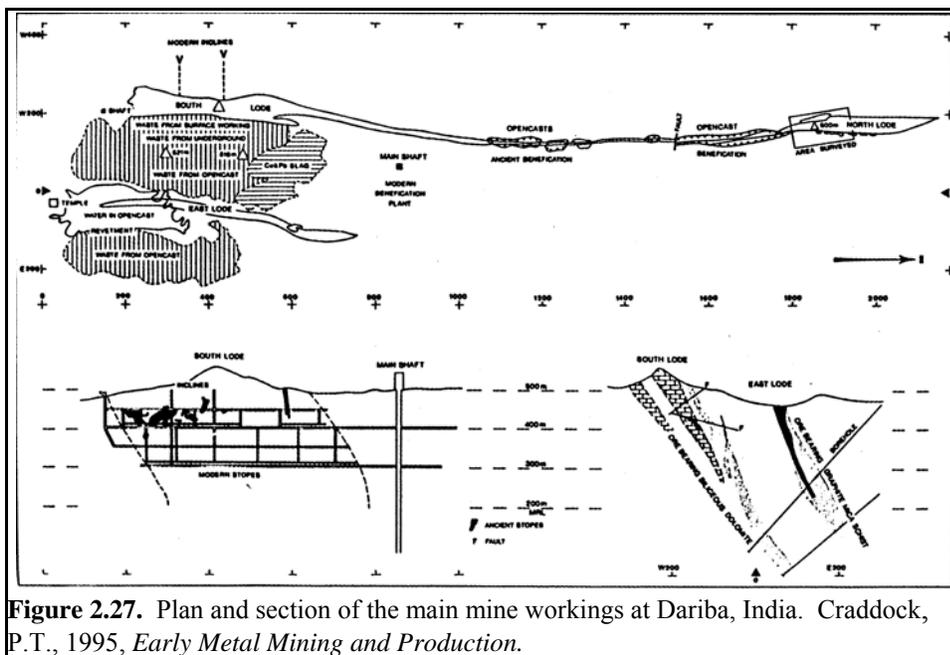
The mines were worked by setting fires within the tunnels to shear off stone, leaving behind a diagnostically smooth tunnel surface. In antiquity the mines were worked to 100 m below the water table. Working beneath the water table was feasible when the geologic layers were non-porous but became a problem when the miners moved into the more porous layers. Legend states that a goddess flooded the mines when the miners became too greedy. The water was bailed out.



**Figure 2.25** The State of Rajasthan in northwestern with the red dots marking lead and zinc mines. The green square shows the approximate location of prehistoric Mohenjodaro.



**Figure 2.26:** The Zawar region of Rajasthan State, India its mines. P. T. Craddock, 1995: *Early Metal Mining and Production*.



**Figure 2.27.** Plan and section of the main mine workings at Dariba, India. Craddock, P.T., 1995, *Early Metal Mining and Production*.

## Spain: Rio Tinto and New Carthage

In Figure 1.3 the fall of Greek silver production followed by the rise of Roman silver production is clearly visible in the pollution of the arctic ice with lead. The bulk of the silver used by Rome was produced in Spain, as can be determined from both historical records and the isotopic composition of lead in the Arctic ice.

The silver mines in Iberia were worked as long ago as Bronze Age. The Bronze Age slags contain some lead (1.37%) (Allan, 1970; Blanco and Luzon, 1969; Tylecote, 1976). The lead in the slag contains about 0.06% Ag, suggesting that the Iberian mines had silver content of 600 g/ton (21.16 oz/ton).

The mines of Spain were apparently first

empties at Tartessus.

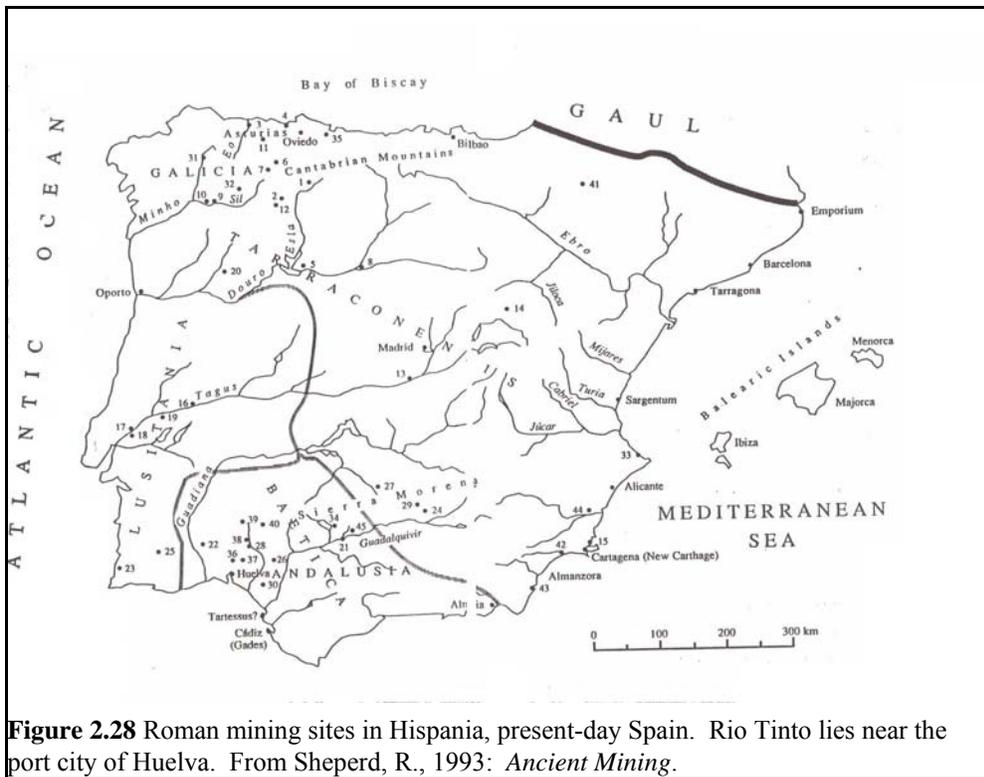
According to legend, Phoenician sailors followed an oracle to establish a colony at the Pillars of Hercules (Strait of Gibraltar). The Phoenicians founded Gadir (Cadiz) at an early date (according to the Romans about 80 years after the fall of Troy) and called the peninsula I-schephan-im (later known as Hispania). The Phoenicians defeated the Tartessians for control of the mines. With the defeat of the Phoenicians by the Assyrians and the Babylonians, the balance of Phoenician power shifted to Carthage. (See, Figure 2.28 for the Mediterranean trade routes at the time of the Roman Empire and for the location of Carthage.)

Carthage defeated the Greeks in the Battle of Alalia off Corsica (535 BC). This victory made

Carthage dominant in the Mediterranean and gave it control over the Straits of Gibraltar. By using a then-modern technology (the battering ram) Carthage gained control of the silver mines at Gadir. The country's rich mineral wealth and its strategic location brought it into conflict with the growing Roman Empire. Rome's first expansion was through the Italian peninsula. The capture of the peninsula's southern end, including Sicily, brought Rome into conflict with

Carthage which was just across the Mediterranean. Roman capture of the eastern edge, Tarentum (circa 280 B.C.) brought Greek culture into the growing empire. During this latter conquest the Romans began to strike coinage. By 269 B.C. Rome was issuing silver didrachma and by 214 B.C. the silver denarius.

During its expansion, Rome fought Carthage three separate times between 264 and 146 B.C. The



**Figure 2.28** Roman mining sites in Hispania, present-day Spain. Rio Tinto lies near the port city of Huelva. From Sheperd, R., 1993: *Ancient Mining*.

exploited by a group of people called the Tartessians. Strabo referred to "The boundless silver rooted springs of the Tartessus River" (Williams, 1996), p. 18 (Figure 2.28). Jonah was traveling to a place called Tarshish, the source of silver. A large bronze cache was found at the mouth of the Rio Tinto. Strabo described the kingdom as containing a series of extensive canals near the Guadalquivir (see Figure 2.28). The Guadalquivir

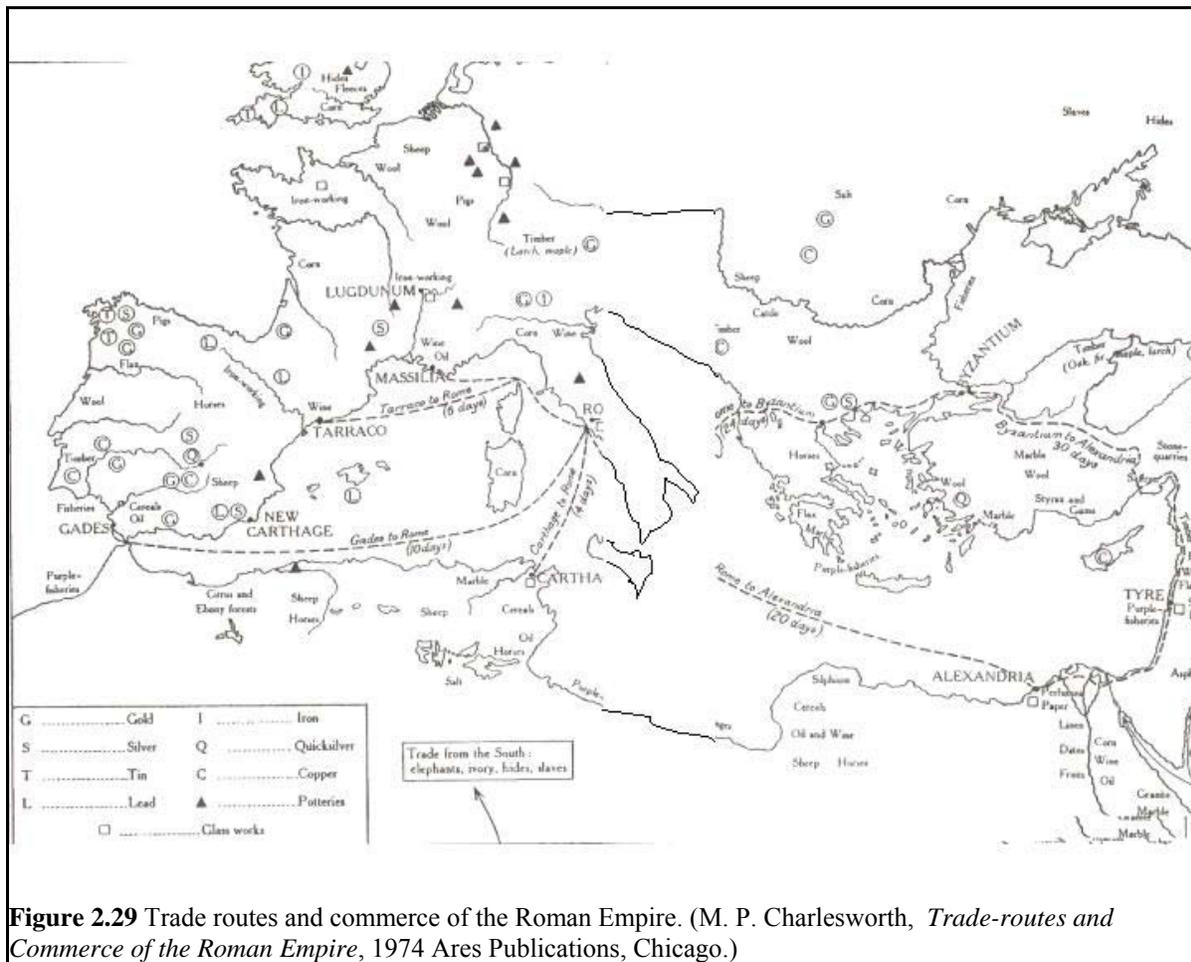
first Punic War (from the Roman word *poeni* for Carthaginian) was won by the Romans 241 B.C. The subsequent social unrest in Carthage led to its 237 B.C. conquest of Spain by Hamilcar and the establishment of full Carthaginian colonies, including New Carthage, or Cartagena. Between the first two Punic wars, Rome turned eastward in expansion. Once the Romans conquered Macedonia in 167 B.C., they prohibited the Macedonians from cutting their own timber. This ban shows just how politically important control of naval and fuel supplies of wood were. While the Romans were occupied in the east New Carthage in Spain began to grow. There Hannibal, the grandson of Hamilcar, sank a variety of mines. Their metals may have enabled his attempt to invade Rome. Full Roman control of the region (over the shattered remnants of Hannibal's forces and the indigenous Celts) did not take place until the first century A.D.

Following the Roman conquest the Iberian

Peninsula swarmed with prospectors who took on the Carthaginian mines. The financing of the Empire from the Spanish silver mines consumed 500 million trees in four hundred years of operation (Perlin, 1989), p. 125.

Salkield estimates 42 tons of charcoal were used daily during the 500 years the mines were in operation (Salkield, 1987).

By the time production peaked at the end of the first century A.D., the Emperor Vespasian needed to promulgate laws that restricted wood use to smelting. Wood for bath houses was forbidden "except for the ends of branches". By the end of the 2nd century A.D., wood supplies were so poor that mine production declined, despite the richness of the ore that remained. The Roman deforestation of the Iberian Peninsula resulted in enormous soil erosion. This erosion buried the city of Tartessos and moved the coastline away from Roman towns of Italica and Hispalis (Sevilla). Hispalis was a port city during the



**Figure 2.29** Trade routes and commerce of the Roman Empire. (M. P. Charlesworth, *Trade-routes and Commerce of the Roman Empire*, 1974 Ares Publications, Chicago.)

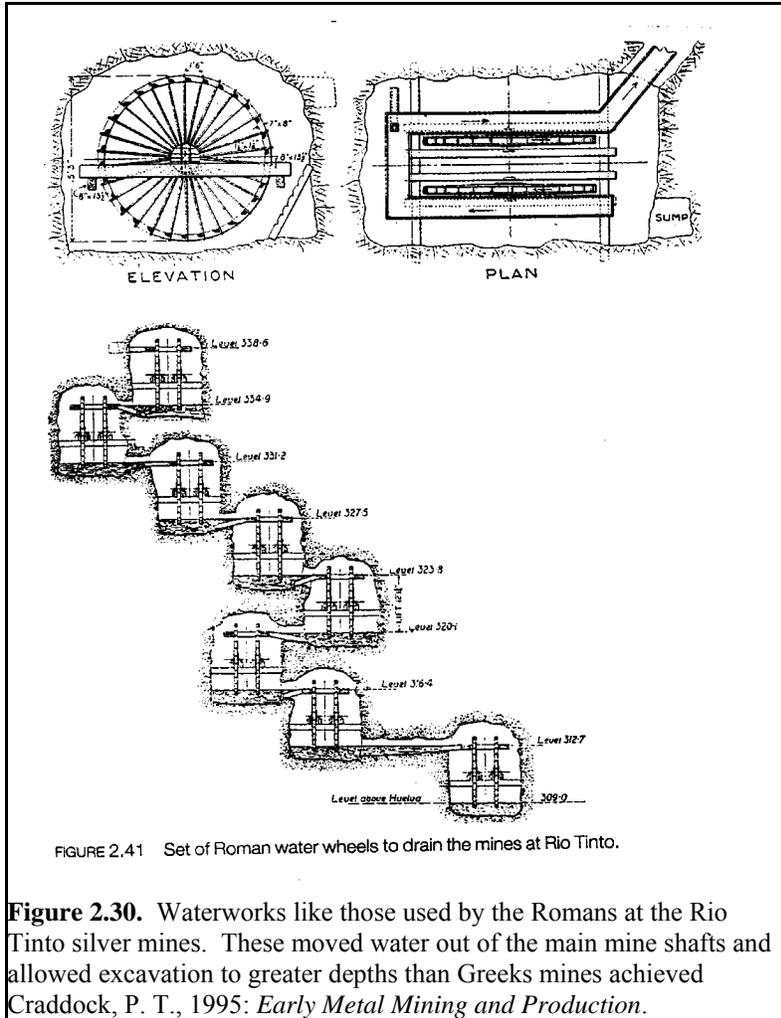


FIGURE 2.41 Set of Roman water wheels to drain the mines at Rio Tinto.

**Figure 2.30.** Waterworks like those used by the Romans at the Rio Tinto silver mines. These moved water out of the main mine shafts and allowed excavation to greater depths than Greeks mines achieved Craddock, P. T., 1995: *Early Metal Mining and Production*.

Roman times, but after the erosion the town was inland.

Roman need for fuel grew with the metal and glassmaking industries. Glassblowing was developed during the time of Julius Caesar, and soon became an important domestic commodity. Italian glass manufacturers clustered just north of Naples and created a large demand for wood. Similarly, potters required a large amount of fuel. The decline of forests in this region pushed industry out of central Italy. Roman potters were very active in 100-0 B.C., but declined by the second half of the first century A.D. They were supplanted by French potters. Glassworking also migrated from Italy to southern France and the Rhone Valley at the same time.

By the end of the 2nd century A.D., silver production slowed because of fuel shortages. The currency was ultimately debased by dilution of the

silver with copper. At the end of the third century A.D., Rome's currency contained only 2% of its original silver. Septimius Severus added 20% more alloy to the silver coinage. At the end of the third century A.D., the currency contained was 98% less silver than the original (Perlin, 1989), p. 126. Table E.1 shows the metal content of Roman coins during this time period (Tylecote, 1976), p. 61.

Typical mining practices in Spain are well described by Pliny the Elder in his *Natural History*. Gaius Plinius Secundus was born at Novum Comum in northern Italy about AD 23 during the reign of Tiberius. During the 30s A.D., he was educated under the soldier and poet Publius Pomponius Secundus. He began his army career in the province of Germany at the age of 23 or 24. He returned to Rome in 59 A.D. at the age of 39 or 40, intending to practice law. In 73 A.D., he became procurator of Spain as well as other parts of the Roman Empire. Because of his wide travel he was able to create a good record of the Roman world. When Vesuvius erupted in 79 A.D., Pliny tried to observe the volcano at close quarters and was killed by sulphurous fumes.

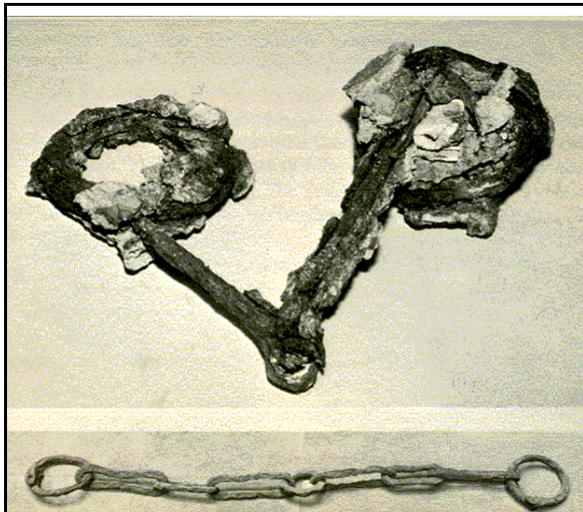
Pliny noted that the Carthaginian shafts made by Hannibal were still in existence 300 years later.

The main lead mines in Spain that he mentioned are *Metallum Salutariense* and *Antonianum* [Pliny, 1938-1963 #309], p. 158. Pliny mentions several Spanish mines (XXXIV:xlix, xlvii, xxxi) which involved lead production: Canabria and the Ebro Valley, Baetica (Huelva), and New Carthage. The mineral deposits of the Huelva Province contained sulphide deposits with up to three percent combined lead and zinc (Rothenberg and Blanco-Freijeiro, 1981), p. 34 and a larger amount of copper. New Carthage was important both as a silver and a lead mine (Healy, 1978). The mine south of New Carthage (Caba de Gata) contained slag of 10-12% lead. Inscribed lead pigs have been found at Orihuela near Cartagena (Tylecote, 1976), p. 61, (Domergue, 1966).

Pliny comments on the relationship between lead and silver: (Natural History, 95)

*Let me speak now about silver, the next source of madness in men. Silver is found only in deep shafts. It does not advertise its existence, having no shiny particles such as are seen in the case of gold. Its ore is sometimes red, sometimes the color of ash. It can be smelted only with lead or the lead mineral called galena, which is found mostly mixed with veins of silver. When cupelled, part of the ore precipitates as lead, while the silver floats on the surface like oil on water.*

96. *Silver is found in very nearly all the provinces, but the best comes from Spain, where together with gold it occurs in barren ground and even in the mountains. Wherever one vein is found, another is subsequently discovered not far away. Indeed, this happens with almost every metal and is apparently the reason for the Greek use of the term metalla (ta met' alla: one after another). It is a remarkable fact that shafts begun on Hannibal's initiative all over the Spanish provinces are still in existence; they are named after their discoverers. One such mine, known today as Baebelo, provided Hannibal with 300 pounds of silver a day. The galleries ran for between 1 and 2 miles into the mountain and along the whole of this distance watermen stood day and night in shifts bailing out water...*



**Figure 2.31:** Shackles used on slaves at the Rio Tinto mines. The right shackle contains the remains of a human foot. J. F. Healy, *Mining and Metallurgy in the Greek and Roman World*. Thames and Hudson, 1978, Plate 37. H.B.S. Bergakademie, Freiberg

98. *The vein of silver nearest the surface is called 'raw'. In earliest times digging stopped when alum was discovered and no further search was made. ...The fumes from silver mines are dangerous to all animals but especially to dogs.*

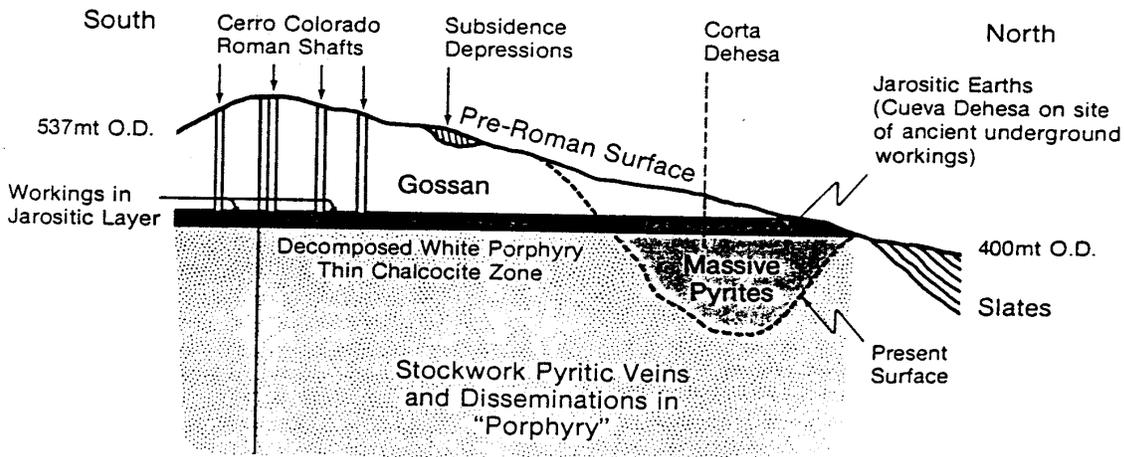
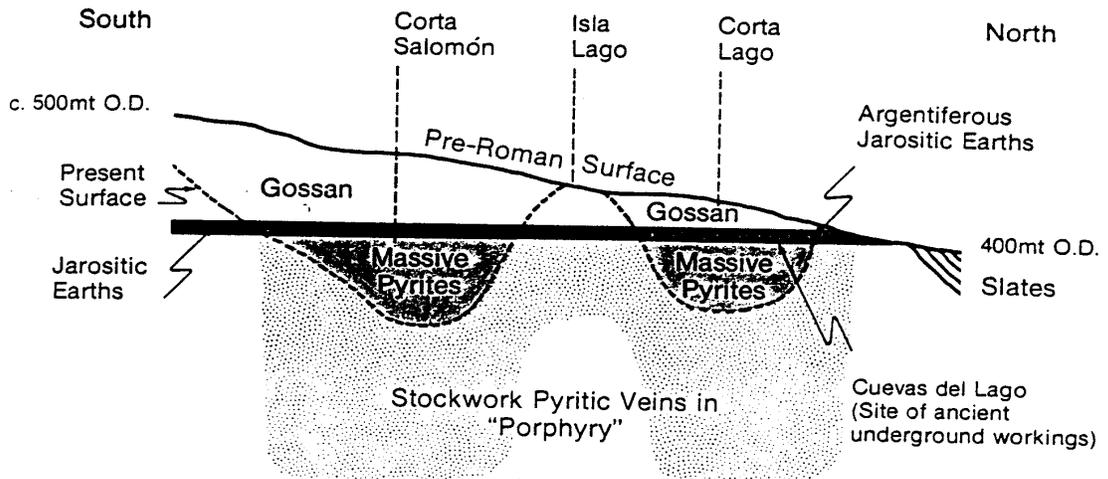
Pliny's description shows one of the major changes in mining technology from Greek times: the Roman shafts were so deep that problems in ventilation and in water removal became paramount. The Romans solved these problems with continuous bailing as well as water-moving devices. Figure 2.30 shows a schematic of water removal devices like those the Romans used at Rio Tinto (Craddock, 1995), p. 7.

Slave labor ran these mines (Figure 2.31). Slaves were acquired by conquest (50,000 on the taking of Carthage, 140,000 Cimbri and Teutons in 104 A.D.) (Glaz et al., 1996), p. 105. Diodorus (XXXVI, 38, III, 2) describes the labor and mechanics of a Roman silver mine:

*At first ordinary private individuals undertook the mining and gained great wealth thereby, since the silver ore was not deep in the ground as was present in great abundance. Later, when the Romans had become masters of Iberia (proto-Berber), a large number of Italians were attracted to the mines, gaining great wealth through their avarice, for they bought a number of slaves and handed them over to the mine supervisor... The slaves, who have to work in these mines, make incredible sums for their masters; but many of them, working far below the ground, exerting their bodies day and night in the shafts, die from overwork. For they have no recreation or recess in their work, but are driven on by the whips of their supervisors, to bear the worst discomforts and work themselves to death. A few who possess sufficient physical strength and a patient equanimity, are able to bear this treatment, but this only prolongs their misery, the immensity of which makes death appear more desirable to them than life."*

(V, 36-37): *These slaves have made openings in various places and by going deep into the earth they*

## Diagrammatic Sketches of Pre-Roman Conditions at Rio Tinto



**Figure 2.32:** Pre-Roman conditions at Rio Tinto showing the various mine workings. Salkield, L. U., 1987, *A Technical History of the Rio Tinto Mines*.

have discovered ground traversed by veins full of gold and silver. Advancing forthwith a distance of several furlongs, not only in length but in depth, by means of

pits that they have sunk, and extending the subterranean galleries in different directions, sometimes transverse, sometimes oblique, they have

*followed the ore wherever it went, and at last, from the bowels of the earth, they have brought to daylight these precious minerals, a source of profit to their masters.....Sometimes, however, when the workings penetrate deeply they encounter streams of water that flow underground, but they succeed in overcoming this difficulty by diverting the flow by means of transverse drains; and as the hope of a great profit, that is never disappointed, does not fail to inspire the operators, they never lose heart; and so finally they achieve their purpose. For draining the water they use also a method still more extraordinary; this is the Egyptian screw, invented by Archimedes of Syracuse when he was traveling in Egypt. These screws raise the water by a continuous movement to the outlet of the gallery, drying the bottom of the mine and making it possible from there to extend the workings comfortably. The art that directed the construction of the machine surpasses all that one can say of it. The Egyptian screw is able,*

*with ordinary effort, to throw up, in a marvelous manner, an immense volume of water; and it draws easily from great depth a stream that if pours forth at the surface of the earth.*

The Rio Tinto mines produced of 16 million tons of slag during Roman times (Salkield, 1987), p. 137. Such production removed massive amounts of earth as shown by the pre-Roman and Roman topography of the mine (Figure 2.32). In Figure 2.32 we see that Roman mining removed material above the pyritic layer and left the pyrite layer exposed to air. The presence of large amounts of exposed iron created conditions in which iron oxidation and reduction further solubilized other ores by converting metal sulfides to metal sulfates, coloring the runoff water of mine, hence the name Rio Tinto (Figure 2.33).

Silver production of silver fell off as either a cause or a consequence of the Roman Empire's decline



Figure 2.33 The water of Rio Tinto is pH 2.3 and contains 300 ppm Cu. The copper is solubilized from the ore by the presence of iron. Photo with permission of Doug Rawlings.

(Figure 1.3). The mine shafts were destroyed during the advance of the Vandals. They were filled with debris and left unused until the invasion of the Berbers from North Africa and the establishment of the Cordoba Caliphate.

With the Muslim occupation of Spain (700s A.D.), some of the mines were again opened, particularly the mercury mines. In 1551 a new, rich silver-lead mine at Guadalcanal near Sevilla inspired the King to establish a commission charged with locating similar ore deposits. In 1556 Francisco de Mendoza, commissioned by Philip II, in turn delegated Diego Delgado, a priest, to visit the area. Delgado “discovered” the Rio Tinto mines. Despite his enthusiastic, lengthy letters, he was unable to create royal interest. In one letter he describes the polluted state of streams issuing from the mines:

*We found another cave called Cueva del Lago (Figure 2.32), from which a stream, Rio Tinto, escaped the stream, being named so because of its constantly colored appearance -evidently springing from a body of mineral -of iron and copper.....In it no kind of fish or any sort of life can exist, neither may persons, nor animals drink of it with impunity, nor can it be utilized for any of the ordinary purposes of life. It has nevertheless several curious and meritorious properties. If any person drink a small quantity of this water he will be relieved if troubled with internal difficulty arising from the presence of anything like 'hydotids'; it is also reported to be highly curative of some disorders of the eyes and of cutaneous ailments such as 'herpes'. ... (Nash, 1904).*

Despite the best efforts of the priest, the mines remained unused until the mid-1850s when changes in metallurgy and in the metals market again rendered them profitable. In 1873 the Rio Tinto Company was formed to work the copper tailings. Most of the holdings were sold in 1954 and in 1962 the company merged with the Consolidated Zinc Corporation to form the Rio Tinto -Zinc Corporation (RTZ). The Consolidated Zinc Corporation was formed in 1905 to work with the zinc bearing tailings at Broken Hill Mines in Australia (see later in the Chapter). From 1962 to 1985 RTZ diversified into allied chemical companies. Between 1988 and 1995 the company divested from its diversified holdings to concentrate on mining again and reorganized into Riot Tinto plc and Rio Tinto Limited ((Tinto, 2003)).

## England

Celtic Britain was invaded by Caesar in 55 and 54 B.C. and conquered by Roman Emperor Claudius in AD 43. On invasion the Romans discovered a region which had a long established history of lead production (Davies, 1979), p. 141. The lead in England was so plentiful, Pliny writes, (xxxiii, 164)

*The lead that we use in the manufacture of pipes and sheets is mined with considerable effort in Spain and the Gallic provinces; in Britain, however, it is found on the surface in such large quantities that there is a law limiting production.* (xxxiii, 164)

Production at Mendips was initiated only 6 years after the Roman conquest. Romans exploited British lead mines (Figure 2.34) such as Mendips in Wales using sulfide ore technology, although those mines were not high in silver. The Mendips lead veins extend from Wells to Weston (Tylecote, 1976), p. 61. Lead silver-free deposits were worked in Derbyshire from AD 117-138.

The Romans kept track of the smelted lead. It was put into forms known as a pigs. Each pig was stamped with the maker's name, the name of the mine from which it was obtained, and sometimes with its purity. One pig found in Hampshire in 1783 was stamped

NERON.AVE.EX KIAN III COS BRIT  
EX ARGENT.CNPASCI

indicating that the pig had been produced at the time of Nero (60 A.D.) at Welsh mines.

The lead was used in its own right, not just as a byproduct of silver. The content of the slag heaps from various Roman mines is shown in Table E.9 (Tylecote, 1976), p. 61. Technology was similar to that used in Spain. Miners used induced drought shaft furnaces a meter or so high.

Lead mining continued to be a major resource for Britain. Lead was apparently mined and exported for money to pay the tax imposed by the Danes during the Saxon period (Smith, 1986).

A census of resources after the Norman Conquest of 1066, known as the Domesday Book, lists seven lead smelters.

Following the Norman Conquest, mineral exports from England increased by tenfold. In the 12th century, 100 carloads of lead were exported from Newcastle to Rouen in France. By the 14th century, King Edward IV's time, an estimated 10,000 people employed in Mendip. Women and children were employed as ore



**Figure 2.34:** Areas of Roman Britain and possible mining areas. Lead is concentrated in central and western England. Robert Sheperd, 1993, *Ancient Mining*.

dressers. By the 17th century, half of all English exports were lead and tin (Tylecote, 1976), p 96.

Even during this period the smelting operation was “primitive”. In Westphalia

*they heap up two wagon loads of charcoal on some hill-side which adjoins a level place*

as Agricola noted in his *De Re Metallica*. A layer of straw is placed on top and on this is

*laid as much pure lead ore as the heap can bear; then the charcoal is kindled and when the wind blows, it fans the fire so that the ore is smelted. In this way the lead, trickling down from the heap, falls on to the level and forms broad thin slabs.*

These were set on hill tops not only for better drought but also because the fumes killed vegetation.

The major centers of production during the 12-13th centuries A. D. were in Cumberland, Yorkshire, Northumberland, Derbyshire, the Mendips, and Shropshire. Even well into the mid-17th century, half of all English exports of Sn or Pb (Tylecote, 1976).

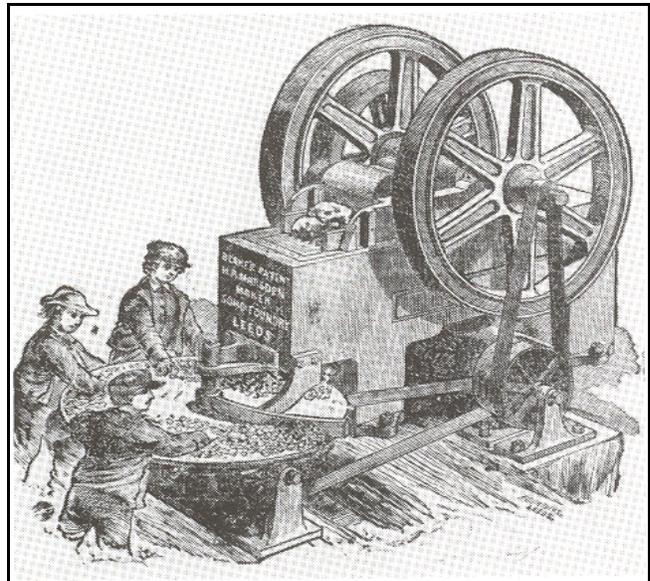
In Wales (Figure 2.35) lead was mined by independent individuals who claimed mineral rights (*meers*) for a royalty or percentage of output in a procedure that followed early Saxon law (Willies, 1999) (Clough, 1980; Hunt, 1970). The rights to claim a site, manner in the claim was displayed, and the settlement of disputes over such claims in Yorkshire was recorded by the mining claim judge in 1653. The review of the law was written in verse as a means of allowing the miners to remember the code (Manlove, 1653):

*By custom old in Wirksworth Wapentake,  
If any of this nation find a Rake, Or sign, or leading to  
the same; may set  
In any Ground, and there Lead-oar may get:  
They make crosses, holes, and set their Stowes,  
Sink Shafts, build Lodges, Cottaghs or Coes.  
But churches, houses, gardens all are free  
From this strange custom of minery....*

The bulk of lead removed was from easily exploited veins which these miners worked in 6 hour days. The days were short as the miners were commonly smallholder farmers as well. By the early 1700s most of the easily found high grade lead veins had been exploited and the remaining lead was either of a deeper depth, requiring water removal, and/or of lower quality. As a result greater capital was required

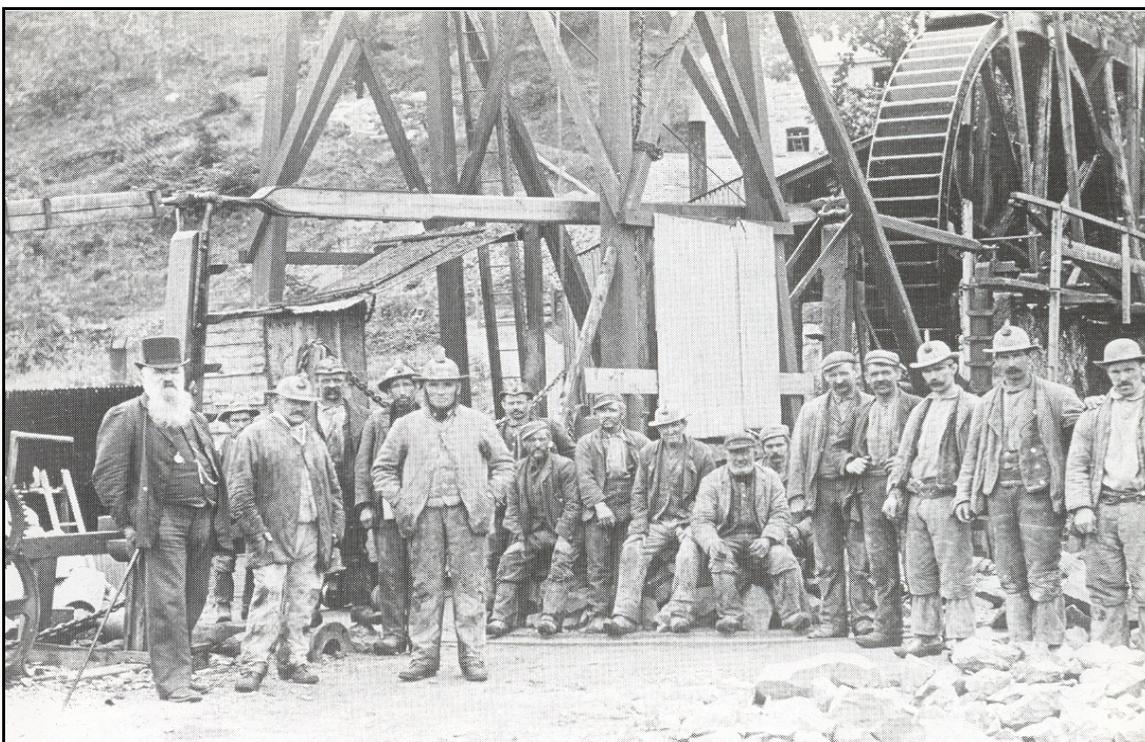


**Figure 2.35.** Map of Southwest Wales. The town of Aberystwyth lies on the western coast, center.

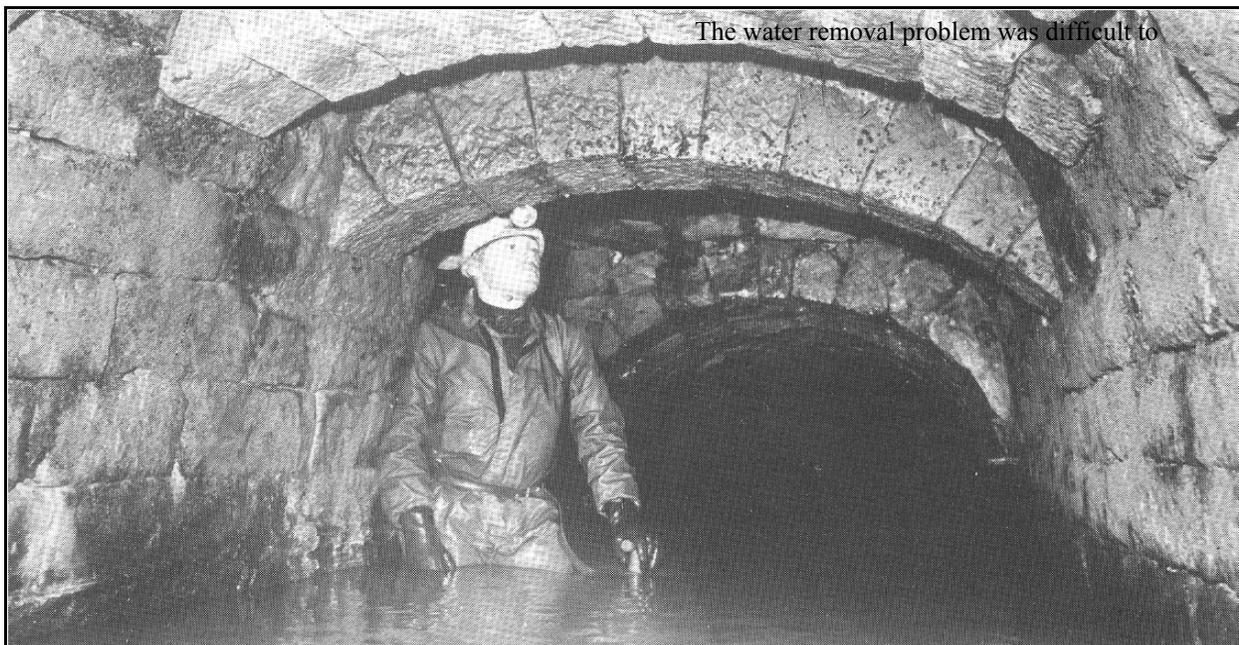


**Figure 2.36.** As ore became less concentrated and pure with increased mining, ore was sorted prior to smelting at the surface. Workers involved in sorting, known as dressing, were often children. Source, Lynn Willies, *Lead and Leadmining*, 1999.

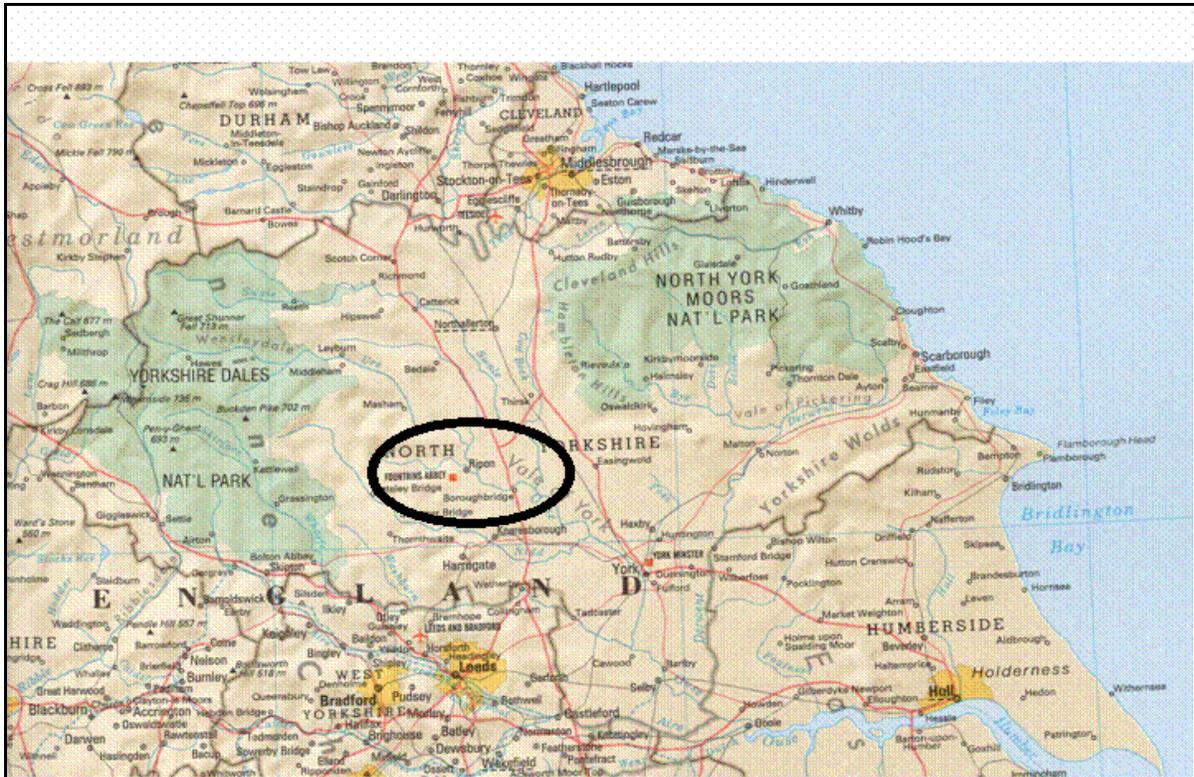
and consolidation of mining began.



**Figure 2.37.** Miners at Trecastell Mine, Conway, North Wales. The miners have tallow dips or candles on their hats. Note the water wheel behind for removing water from the mine. From Lynn Willies' *Lead and Leadmining*, 1999.



**Figure 2.38.** A "sough" at Hillcarr, Derbyshire built in 1766-1783 for water removal. The sough is 4 miles long. From Lynn Willies' *Lead and Leadmining*, 1999.



**Figure 2.39.** Map of the Yorkshire area of mining in England. Fountains Abbey is circled.

solve because, in general, the topography of England did not lend itself to gravity driven water flow nor to wind power. Power removal of water was first used in 1717 in Derbyshire (Figures 2.37 and 2.38). Removal of water allowed exploitation of deeper ore veins and the largest productivity of English lead mines ensued with Yatestop producing 3,000 tons of lead/year in the early 1700s. The largest financial backer for lead mining was the London Lead Company, a Quaker concern which began moving into North Wales, Derbyshire and the Pennines in the early 1700s.

As consolidation of the industry accelerated in the 1800s labor strikes over the length of the working day occurred. Companies moved to enforce 8 hour work days over the prior 6 hour day which made subsistence farming possible. Under company consolidation workers bid against each other for work every 7 to 8 weeks. They supplied their own materials and undertook all of the risk involved in the mining process.

As the ore became less concentrated sorting no longer took place within the mine shaft by the miner

but was “dressed” by workers above the mine. These workers were often children (Figure 2.36).

A similar change in lead mining activity took place in the Swaledale area of Yorkshire, England (Figure 2.39). Lead mining in that region was carried out by the Romans (Figure 2.32) and was also noted under the Normans. ~550 tons of lead were exported from York between 1179 and 1183 A.D. to various abbeys in England and France for roofing material (Lead Mining in Yorkshire).

In 1145 Count Alan of Brittany gave Jervaulx Abbey the right to mine lead, while Roger de Mowbrey gave lead mining rights to Fountains and Byland Abbeys in Stonebeck Up and Down (Coldstones Mining area). The abbeys had a variety of commercial conflicts over lead with the Company of Merchant Adventurers in York. The monastic rights were bought from King Henry VIII resulting in a first phase of consolidation of mining in England.

The enhanced rights to mining made bringing in experts on mining from Saxony and construction of larger smelters feasible. A second increase in



**Figure 2.40.** Lead mining remains of the Middle Vein, Grassington Moor, Yorkshire. Source: Raistrick, A., 1975.

capitalization occurred in the early 1700s as gunpowder



**Figure 2.41:** Drilling with compressed air in 1912 at the Homestead Mine in S.D. Postcard (Author.)

was introduced into mining. A further consolidation of interests occurred as some York families were dispossessed of lands during the Jacobite rebellion of 1715. Mining output eventually slowed in the late 1700s as the mines approached the water table. Application of steam engines in pumping allowed lead mining to again become profitable in the late 1700s. A second wave of property consolidation also occurred allowing a single landowner to control all rights to a single lead vein making exploratory investments such as tunnel building for water drainage less risky.

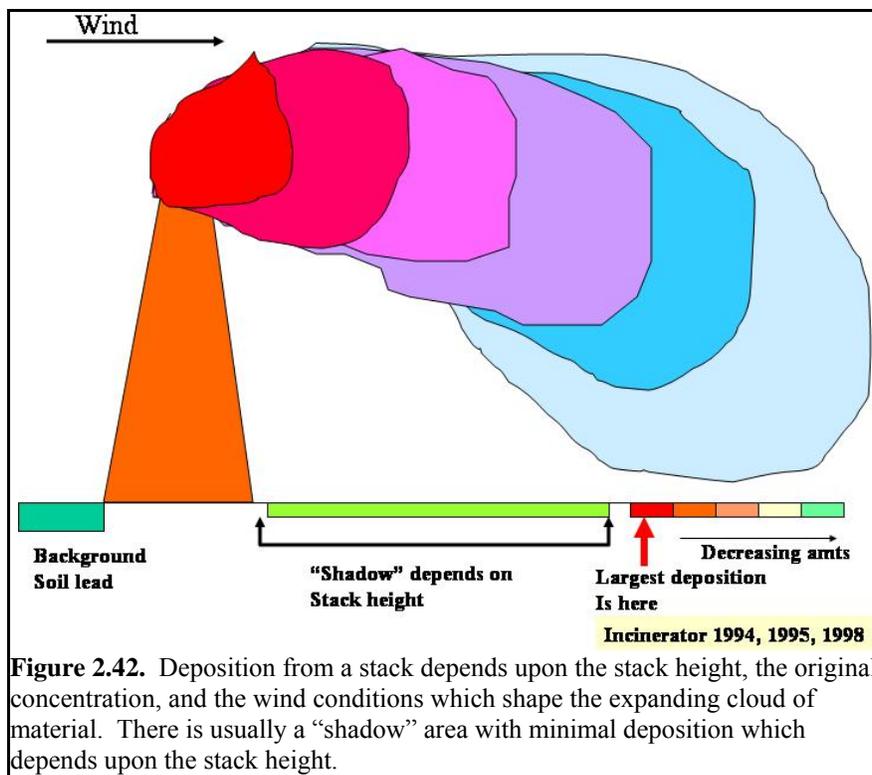
The Duke of Devonshire invested in such a project which lasted 30 years. With large amounts of lead from a single supplier mills and smelters

could count on regular supply of ore and invested in even larger facilities.

In order to deal with the increased lead fumes and lead dispersion large flues (partially horizontal chimneys) were run up hillsides to vertical chimneys on the crest. Gases condensed in the cool underground flues, reducing the dispersion of lead from the chimneys.

Lead mining died out in the 1880s as the subsurface veins became well worked. With the introduction of new engines, compressed air, and dynamite, some veins became commercially viable again in the 1910s and 1930s (Figure 2.41). By 2000 lead mining in England was relegated to the status of a byproduct of fluorspar, barite, and calcite mining. In addition, recovery of some minerals necessary for the computer industry have resulted in disturbances of the early slag heaps (Clegg, 1999).

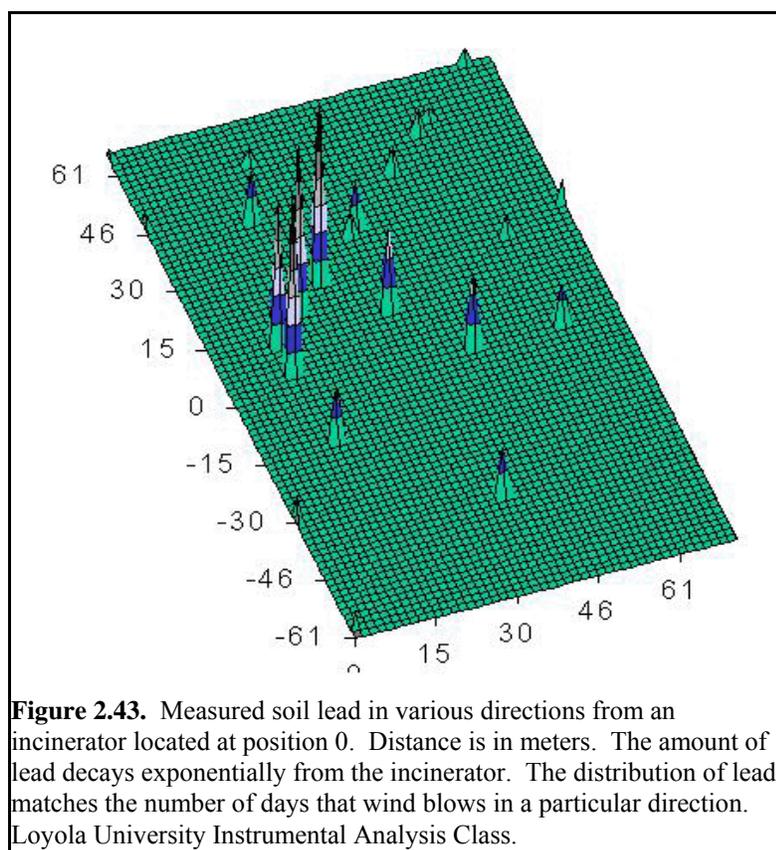
The slag heaps were not the only bequest of the mines (Figure 2.40). Above we noted that the Romans often placed their smelters on hill tops to minimize the toxicity of the fumes from the smelters. The output from the smelters was distributed away from the smelter site in ever decreasing amounts which can be modeled as an exponential decay (Figure 2.42). The remains of the early lead mining activity affects agricultural practices today. Clegg notes that sheep grazing in lead contaminated pastures of Derbyshire have a high loss of lambs (Clegg and Rylands, 1966). Other workers have noticed osteoporosis of young



lamb in the Southern Uplands of England (Butler et al., 1957).

The first report of mine activity on lead deposition in soils affecting crops is from 1919 by Griffith (Griffith, 1919). He investigated 1908-1913 complaints of soil infertility of farmers in Aberystwyth (Wales, Great Britain) site of Roman/British lead mines. It was not until 1971 that Alloway and Davies continued the work and indicated that the Ystwyth river valley contained 90-2,900 Fg Pb/g of soil as compared to a valley unaffected by mining (24-56 ug/g) (Alloway and Davies, 1971). Similarly the mining area of Missouri was found to have soil lead of 2,200 Fg/g (Davies and Wixson, 1985) Appendix G.1. The contamination is primarily localized, with an exponential decay from the source (Lagerwerff et al., 1973).

Similar exponential decay occurs near municipal waste incinerators, as mapped by the students of Loyola University at the Chicago Northwest incinerator (Figure 2.43).



## Germany

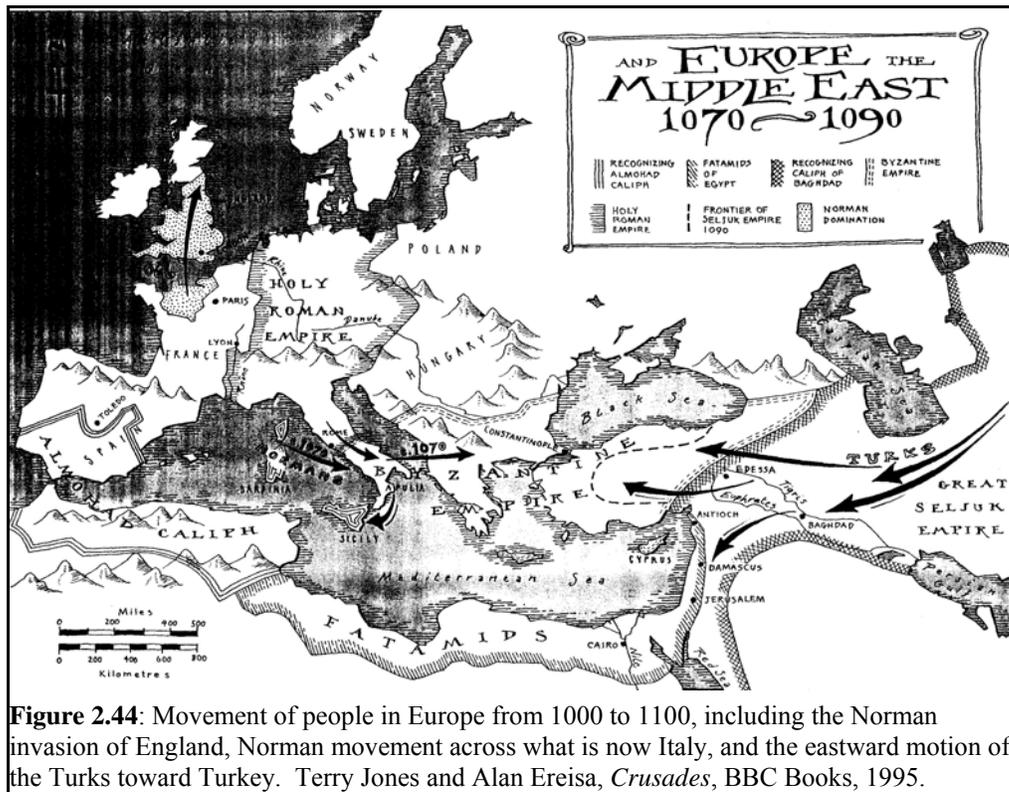
After the fall of the Roman Empire, various tribes were on the move in Northern Europe, leading to conditions unsuitable for mining. Some silver mining activity of the Harz Mountains by Saxons, Avars, and Czechs is noted in records of the 700s, but the mining was not on a large scale (Boyle, 1987). The Avars, a nomadic tribe from Central Asia ruled by Khagan Bajan (565-602), worked mines in Kremnitz, Vorrspatak using fortified rings or enclosures. Although gold was desired with the development of the Charlemagne founded empires, it was scarce and silver became the coin of the realm (911-1024). Not until 1253 was the first gold coin struck: the Florentine gold florin.

Paralleling the Norman invasion of England (1066) were other expansionist movements including the *drang nach osten*, or eastern movement of the German people from 700-1100 A.D. (Figure 2.44). The Normans and Franks had developed warfare to a high art. They were responsible for the “nearly” invincible armored knight. They sought outlets for this technology and warrior class. Lured by the riches of

the East, and comforted by the thought that this was a holy war, the Normans moved to establish kingdoms in Italy, Sicily, and the Holy Land. In 1099, during the First Crusade, the Norman Tancred took Jerusalem. He captured the Dome of the Rock during Friday prayers, slaughtering so many worshipers that one crusader reported picking his way through knee-deep blood and bodies. In addition to purging of the Holy Land, the Normans acquired:

*more than forty silver candelabra, each of them weighing 3600 drams, and a great silver lamp weighing forty-four Syrian pounds, as well as a hundred and fifty smaller silver candelabra and more than twenty gold ones, and a great deal more booty* (Jones and Ereisa, 1995).

The westward flow of wealth from the Muslim countries and a growing population stimulated trade and mining (Clapham et al., 1987), p. 699. Some of the crusades were taken against the Muslims in Spain. Others constituted expansion to the Slavic, non-Christian east. During this expansionist movement, silver was discovered near Goslar, Saxony, Germany in



**Figure 2.44:** Movement of people in Europe from 1000 to 1100, including the Norman invasion of England, Norman movement across what is now Italy, and the eastward motion of the Turks toward Turkey. Terry Jones and Alan Ereisa, *Crusades*, BBC Books, 1995.

965. In 1170, silver was found at Freiberg. Wagon drivers passing through that area recognized galena like that in the ore at Goslar. The major silver mining areas were Freiberg (starting in 1170), Annaberg (1496), and Goslar (965), Schneeberg (1471), Marienberg (1520), and Joachimsthal (1576). The *Joachimstaler*, the coin of this last area, was shortened to *thaler*. The word eventually became “dollar.” Major writers of the early silver mining period were Roger of Helmarshausen (“Theophilus”) author of “On Divers Arts” (~1100 A.D.) and a practicing metallurgist, and Albertus Magnus (Saint Albert the Great) (1206-1279), a philosopher of natural history and metallurgy.

With the fall of the Roman Empire, mine shafts for silver deeper than 40-50 feet were destroyed. The mining of iron was technologically less complicated. As iron ore was spread out more widely than silver across Europe, its mining continued unabated. One reason was a continued demand for iron in the production of the stirrup (invented about 200 B.C.) and the Northern European mail armor (starting about 700 A.D.). When conditions were ripe to re-establish silver mining, the prevailing labor laws were affected by local control at the village level of the iron works (Clapham et al., 1987), p. 724. Miners’ social status was comparable to that of town citizens. A serf could be freed for performing mining tasks.

South Germans (Tyroleans) moved into Bohemia at the end of the 12<sup>th</sup> century. During the 13<sup>th</sup> century they began silver mining in the rich Hartz Mountains. The communities of the frontier organized into collective groups (*Gewerkschaft*), but admitted outside members when cash was required (Rosen, 1943), p. 40-42. Through this practice, the original workers lost control of the mines and became wage earners. The Fugger family became large stakeholders in mining by this process. The Fugger mines at Villach employed Paracelsus, the important observer of contemporary metallurgy (1515-1540), for a period of time. The gradually declining status of the miners led them to side with peasants in the Peasant’s War of 1524-1525. With their loss, the guild system of mining ended.

Schneeberg (Saxony) reached its peak production in 1480s. However, most mines enjoyed their greatest prosperity at the time of Agricola (1494-1526) and Paracelsus (1515-1540). Silver output increased between 1460 and 1530 by a factor of five. Three million ounces were produced each year between 1527 and 1530. Holy Roman Emperor Charles V estimated that 100,000 people were employed at the mines.

Mining technology advanced during this period, particularly with respect to energy requirements and water removal. Mines in northern Europe were subject to flooding at 60-100 feet unlike Roman mines, which flooded at greater depths (Clapham et al., 1987), p. 724. Water wheels from the swift mountain streams were used for water removal as well as ore sorting (Figure 2.45), crushing (Figure 2.46).

Mines and mining areas became centers of learning with associated scholars like Agricola and Paracelsus. For example, Agricola who was born Georg Bauer in Glauchau, Saxony in 1494, he studied philosophy, medicine, and natural sciences. In 1526 he was appointed the official town physician at the silver mining town of Joachimsthal, Bohemia. He describes the miners as working 7 hour shifts. He also notes clear cases of arsenic poisoning, recommends the use of primitive ventilators, and describes local means of avoiding the mine demons (fasting and prayer.)

These spirits live on in folk and fairy tales such as that of Snow White. Snow White’s friends are more properly described as gnomes rather than dwarves. Dwarves were cave and cellar dwellers who left the German lands due to the noise of mining:

*When the iron forges and stamping mills were built in the Erz Mountains, the noise drove the Dwarfs out. They complained bitterly about the situation but told the people they would return once the noisy works were removed (Grimm and Grimm, 1981).*

Gnomes inhabited the mines as well as spirits:

*The Little People or Gnomes, look almost the same as Dwarfs, but they are only about 10 inches tall. They have the figures of old men with long beards, dress like miners with white hoods attached to their shirts, and carry lanterns, picks, and hammers. They never harm the miners. And even when they occasionally throw rocks, it’s rare that anyone gets hurt - unless the Gnomes have been angered by abusive language and cursing. They especially like to appear in shafts rich in ore or where the prospects for making a strike are good. Because of this the miners are not afraid of Gnomes. In fact they consider it such a good omen when they appear that the miners work harder and happier.*



**Figure 2.45:** Agricola's depiction of ore sorting by gravity and sieving using water chutes.

- A - workman carrying broken rock in a barrow.
- B -first chute.
- D - Its handles.
- F. Rope.
- H. Post.
- K. Second box.
- M. Third Box.
- O. First Sieve.
- Q. Second Table.
- S. Second Tub.
- V. Third Sieve.
- X. Third Tub.
- Y plugs.
- C-first box.
- E - Its bales.
- G. \_Beam.
- I - Second chute.
- L. Third Chute.
- N. First Table.
- P. First Tub.
- R. Second Sieve.
- T. Third Table.



**Figure 2.46:** Milling operations as shown by Agricola, with wheels are turned by wind, goats, and men.



**Figure 2.47:** Bockleman's Painting of Lead Miners in Europe.

The mine spirits, as verified by Agricola, were not so benign:

*From time to time, deep in the shafts of mines, there appears a gigantic figure clad in the black robe of a monk. He is called Meister Hammerling, or more frequently Mine Monk*

*He frequently appeared in the mine in the Graubunden Alps - especially on Fridays. There he was seen emptying the ores from bucket into another and then back again. The owner of the mine was careful not to object to this activity, and the spirit responded in kind by never causing any trouble. But one miner became upset at this seemingly wasted effort, and he scolded and cursed at the spirit, whereupon the spirit grabbed the man and shook him violently. The miner survived the attack, but from that day on he walked around with his face turned inside out!*

*Then there was this incident in the Anna Mine. Twelve men were working the Rosencranz shaft when the spirit suddenly appeared and breathed on them. All the miners dropped dead on the spot. This explains why this particular shaft, although rich in silver deposits, has never again been worked.*

*In the Anna Mine he appeared in the shape of a steed with a long neck and terrifying eyes, but in the St. George Mine in Schneeberg he appeared again as a black-clad monk. Here he seized an apprentice, lifted him up into a shaft rich in silver deposits, and set him down so violently that the youth injured all his limbs.*

*Another time in the Harz Mountains, the spirit*

*punished a mean foreman who tormented the unfortunate miners. When the foreman was emerging from the shaft, the spirit positioned himself above the entrance where the man could not see him. As the foreman left the shaft, the spirit caught the man's head between his legs and crushed his skull (Grimm and Grimm, 1981).*

A second scholar of the area, contemporary to Agricola, was Paracelsus (1515-1540). Paracelsus' father was town physician in Villach, where the Fuggers of Augsburg owned mines and had a mining school. Paracelsus further studied Galenic medicine (based on the four humors) under Leoniceno. In 1527 he became the town physician in Basel and lectured, under the influence of a nationalistic spirit, in German. After being expelled for his heterodoxy, he wandered the continent. He visited mines and smelter works in Tyrol in 1533 and was employed in the Fugger mines at Villach in 1537-38. Sometime during this period he wrote *Von der Bergsucht und anderen Bergkrankheiten (On miners' sickness and other miners' diseases)*.

Mining in the area declined in the 14th and early 15th centuries. This change was related to a decline in European population as a result of the Black Death. The population decline reduced social mobility and consumption and therefore demand for metal. Many pits were demolished in war. The Hussite Wars (1415-1436) destroyed Kuttenberg, Eyle and Deutsch-Brod. The lessened demand for metal lead to decreased output, which in turn caused shortages of gold and silver. The ruling class then debased the currency. The decline of the Roman mines at Rio Tinto was accompanied by a similar cycle of events.

## Mexico and Bolivia

When Constantinople fell to the Turks, the entire balance of Mediterranean trade was altered. Sea routes to the eastern overland trails now fell under Muslim control. Venice's commercial power was decapitated. Portuguese sailors began looking for an alternative route to the riches. They were propelled in part by the knowledge that gold lay south of the Sahara. Gold trade to people south of the Sahara had been described by Abu 'Ubayd Abdallah al-Bakri of Cordoba (*Kitab al-masalik wa 'l-mamalik*) (Wilks, 1997). Until the discovery of America, the Wangara tribe of Africa was the main supplier of gold to Europe.

The Wangara were traders connecting the source of gold (in the Timbuktu region along the Niger River) with North Africa. It is postulated that 4,000 tons of silver and 800 tons of gold were exported across the desert by Islamic African traders who connected with Venetian merchants in North Africa. Despite the influx of African metal, Europe had shortfalls of coinage material since the imported material was largely sent to China in trade. To directly tap into the gold trade, Portuguese sailors ventured south of the Sahara traveling along the shoreline. In January 1471 Joao de Santaram and Pero de Escobar "discovered" the "Gold Coast" of Africa.

The success of the Portuguese explorers led to major Spanish explorations to the west and to English expeditions to the northeast and northwest. The discovery of the Americas by Spanish-backed Christopher Columbus in 1492 did not immediately bring about an influx of riches. This did not happen until the conquest of Mexico and Peru. Nuggets of superficial ("found", see Figure 2.2) gold and silver had been collected and used by the indigenous population. This hoard was sent to Europe by the conquerors. The initial looted silver from Cuzco alone was about 5,000,000 lbs sterling. The 22,600,000 pesos coined by Mexico City mint between 1537 and 1550 derived from plundered metals (Bernstein, 1964), p. 9.

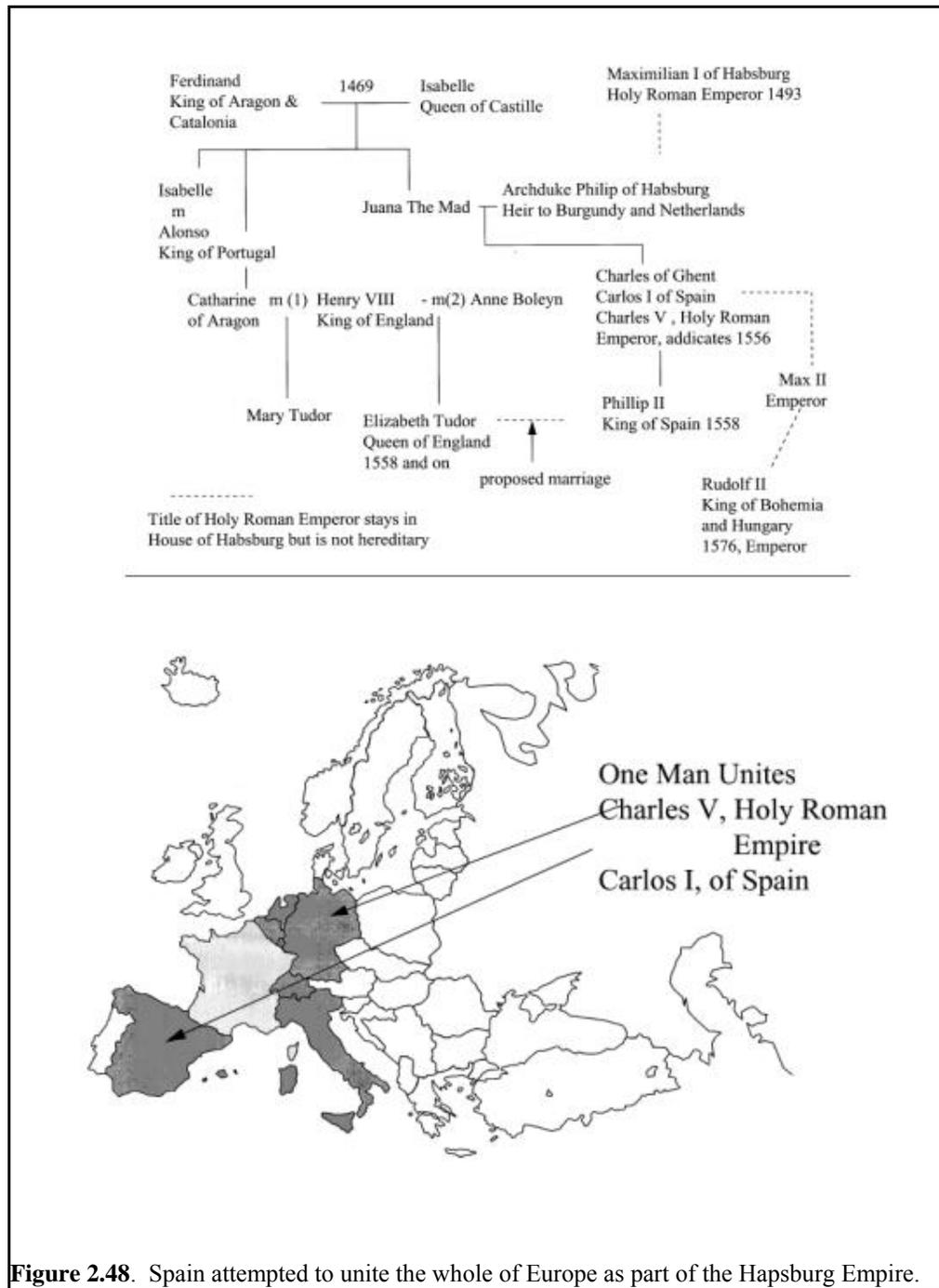
Charles V (also known as Carlos I) and his son Phillip II played important roles in both German and New World mining and alchemical developments. (Figure 2.47 shows their genealogical map). Ferdinand, King of Aragon and Catalonia, married Isabel, Queen of Castille. The marriages of their four children were politically designed. Daughter Isabelle married Alonso, King of Portugal, and Catherine of Aragon married Henry VIII, King of England. They became the parents of Mary Tudor, the short-lived

Catholic queen of England. Daughter Juana (heir to the Castillian throne) married Archduke Philip of Habsburg, heir to Burgundy and the Netherlands and son of the Holy Roman Emperor, Maximilian Hapsburg. The offspring of this match was Charles of Ghent. He became Carlos I of Spain and was elected Holy Roman Emperor in 1519, as Charles II. This single regent united the Netherlands, Burgundy, the Holy Roman Empire (German states), Spain, and the New World (Figure 2.48). He was crowned king of Lombardy and Emperor of the Romans in 1530. His election as Holy Roman Emperor involved Chicago style politics that left him massively in debt. The cost of 850,000 gold florins was raised through the Fugger firm (indebted at 400,000 florins) (Goldwater, 1972), p. 62. To pay the Fuggers, he gave them control of the Almaden mercury mines.

The Almaden mercury mines were first worked by the 4th century B.C. according to Theophrastus. Pliny describes the mine of Sisapo in Baetica. The next reference to these mines is by the geographer Abu-Abd-Alla-Mohamed-Al-Edrisi (Edrisi) in the first half of the twelfth century. Edrisi named them "the mine" or "Al maden." 1,000 laborers were working to a depth of 500 feet at the time of his visit (Goldwater, 1972), p. 38-40. As a reward for the Christian conquest of Spain, the monks of Calatrava received the mines in 1168 and began working them during the reign of Ferdinand III (1199-1252). The mines reverted to crown control in the early 1500s.

The mercury mines at Almaden were an integral part of New World silver exploitation. Rich silver deposits were discovered at Taxco Mexico in 1542 and at Potosi, in Bolivia in 1545. The conquistadors were particularly ill-suited to exploit the mines. They had little or no metallurgical expertise. One of the first acts of the conquistadors in the 1540s was to ask the Spanish king (Carlos II and later Philip II) for experts in silver mining and refining. These early mining ventures were worked with Indian slave labor, which was abolished by 1550, leading to an end of "quick and dirty" mining.

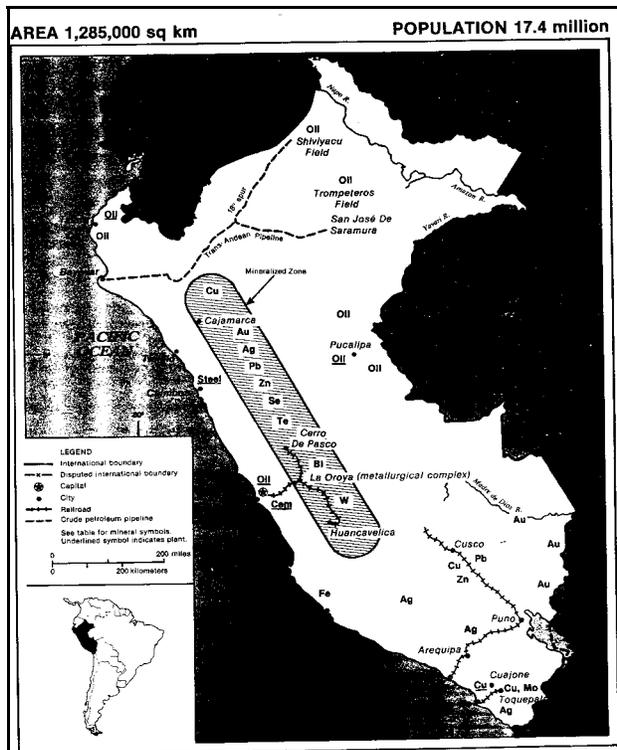
Figures 2.49, 2.50, and 2.51 show the regions of Spanish silver mining in the New World. Most of these mines exploited the oxidized ores at the surface



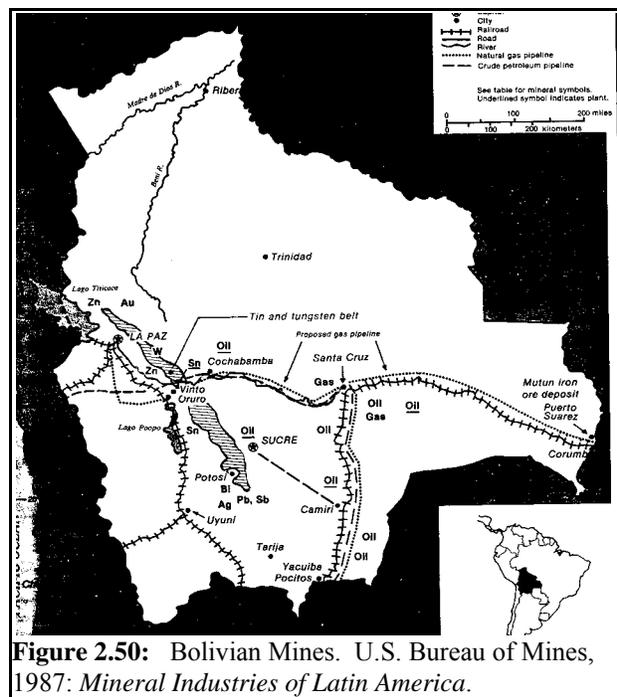
(West, 1997). The conquerors would have needed cupellation techniques to get silver from the reduced sulfide ores. In 1539 a miner at Taxco needed 25 hundredweight of litharge to refine only 75 to 126 ounces of silver. Although the lead was mined at

alternative sites, even so the amount of fuel required made traditional lead cupellation a costly process.

Indian workers would steal pieces of rich silver-lead ore and extract silver using blowpipes



**Figure 2.49** Mines of Peru: U.S. Bureau of Mines, 1987: *Mineral Industries of Latin America*.



**Figure 2.50:** Bolivian Mines. U.S. Bureau of Mines, 1987: *Mineral Industries of Latin America*.

(*soplillos*) or small cupelling furnaces (*cendradilla*) (Figure 2.16). The fumes in the huts often lead to the death of children by lead poisoning. The mining ordinances of the Audiencia of Mexico in 1542 urged mine owners to control this practice (West, 1997). Lead for cupellation came from Zumpango del Rio, Tehuacan, and the Mixteca Alta.

As with the Romans, energy consumption and supply of lead were considerations. In the vicinity of Sultepec and Taxco, oak-pine forests had originally been present. Mining ordinances in 1542 attempted to protect the forests. Viceroy Mendoza warned Luis de Velasco about them:

*In just a few years a large area of forest has been destroyed [near the mines], and it appears that the wood supply will be depleted sooner than the ore. Ordinances have been made regarding the conservation of the forest, and likewise regarding the paths that the Indian workers use for making charcoal, cutting wood, and on the maximum loads that they may carry...(1550)..*

Production was sustained, however, because of a major change in metal ore processing. Al Hamdani, in a mid tenth century text describes recovery of finely dispersed metallic silver with mercury ( ). A thirteenth-century text of Mansur ibn-Ba'ra of Cairo describes this process in detail. Biringuccio writes of the recovery of silver salts in 1540 in his *Pirotechnia*, which he says was a German secret (Smith and Gnudi, 1990), p. 142). Agricola mentions in his text *De Re Metallica* the use of mercury amalgamation for the purification of silver. However, the widespread adaptation of amalgamation, known as the patio process, first took place in the New World. Amalgamation was introduced in the 1550s in Mexico by a Spanish immigrant, Bartolome de Medina, who stated on wrote Dec. 29, 1555:

*I, Bartolome de Medina, do declare that I learned in Spain through discussion with a German, that silver can be extracted from ore without the necessity for smelting it, or refining it, or incurring any other considerable expense. With this information I resolved to come to New Spain. Leaving my home, my wife and my children in Spain, I came to test it, knowing that if I were successful, I would render a great service to Our Lord, and to his Majesty and to all this realm. And having spent much time and money and suffered mental anguish, and seeing that I was not going to be able to make it work, I commended myself to Our Lady and I*

*begged Her to enlighten me and guide me, so that I might be successful and it pleased Our Lady to enlighten me and put me on the right path so that I could make it work (Probert, 1997).*

Medina came from the Guadalquivir River in the area near Rio Tinto near Seville. Rio Tinto, as we have seen, was the site of major Roman silver mines. Seville was given all concessions for trade with the New World and therefore was in contact with the New World. Medina was a successful wholesale trader, a position he gave up to study silver metallurgy, particularly that of “dry” ore. Dry ores consist of  $\text{AgCl}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{Ag}_3\text{SbS}_3$ ,  $\text{Ag}_3\text{AsS}_3$ ,  $\text{Ag}_5\text{SbS}_4$ , and fahls as opposed to “wet” lead/silver ores of galena, cerussite, and anglesite or jarosite sulfate ores. He apparently obtained a dry silver ore from Rio Tinto and taught himself, through experiment, cupellation. Most ores of the time did not approach this quantity.

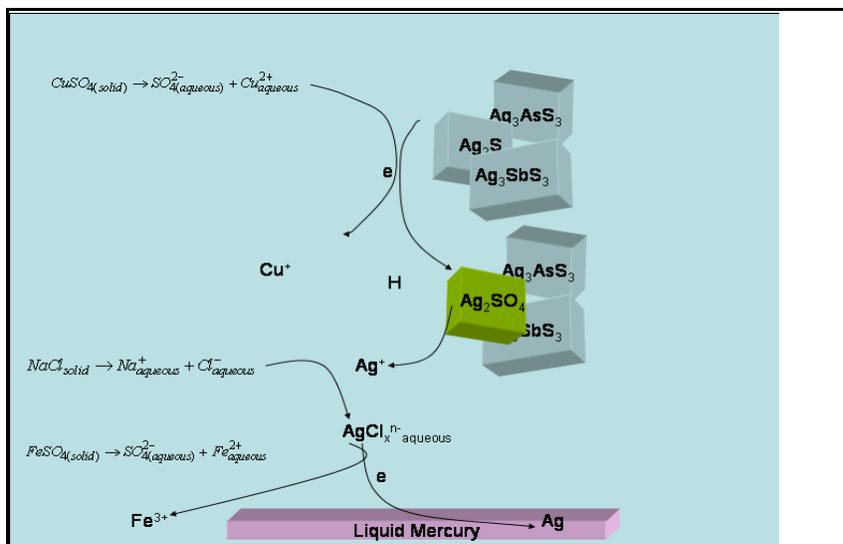
Medina realized that an ore body with at least 200 ounces silver/ton of ore was needed for cupellation. Medina learned from a German, Maestro Lorenzo, about amalgamation:

*Grind the ore fine. Steep it in strong brine. Add mercury and mix thoroughly. Repeat mixing daily for several weeks. Every day take a pinch of ore mud and examine the mercury. See? It is bright and glistening. As times passes, it should darken as silver minerals are decomposed by salt and the silver forms an alloy with mercury. Amalgam is pasty. Wash out the spent ore in water. Retort residual amalgam; mercury is driven off and silver remains.*

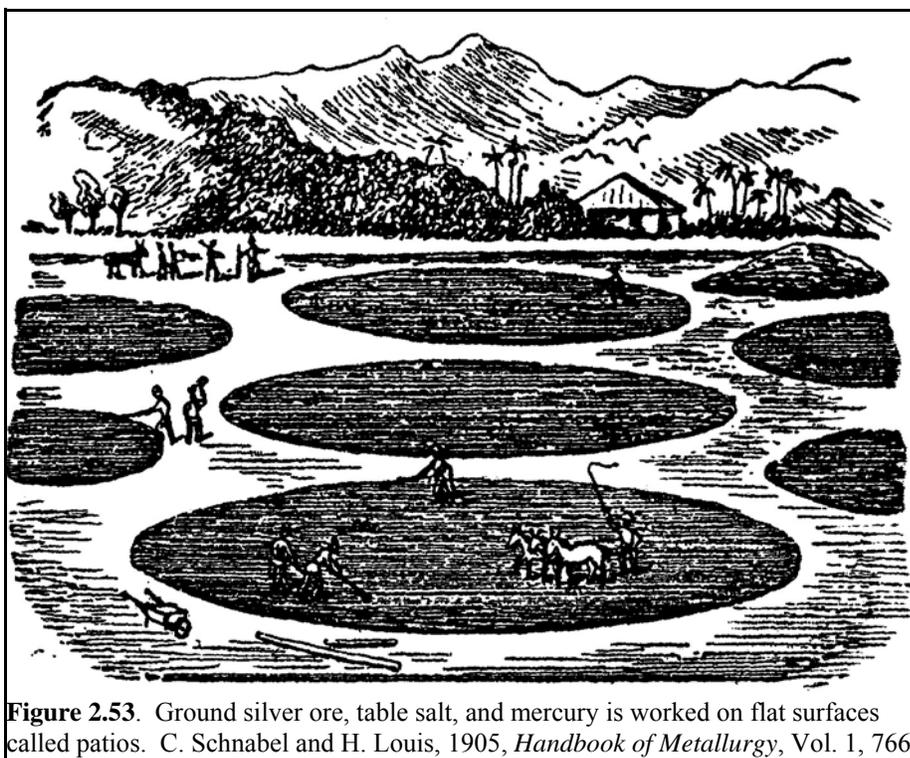
Armed with this new knowledge, Medina set sail for Mexico in 1553. This was a particularly auspicious time because Carlos I (Charles V) was



making war in the Netherlands to prevent its move to independence, and thus was in urgent need of money. Medina set off with a silver rush to Pachuca, where he attempted the amalgamation procedure by using mercury, the “dry” ore, and common table salt. Nothing happened, however. In desperation, Medina recalled that the Rio Tinto ore was also high in vitriol (sulfate). He then tried adding other salts to the process (vitriol ( $\text{CuSO}_4$  and  $\text{FeSO}_4$ ) know as magistral (Ramage and Craddock, 2000), p. 236). The salts help oxidize sulfur to sulfate creating a more soluble metal compound. The presence of chloride also facilitates transfer of the ore metal through the debris to the mercury. Similar oxidative mechanisms have been demonstrated in determining the solubility of mining debris ((Carroll et al., 1998). The mechanism is likely very similar to that for ore bearing brines whose high NaCl content flowing through high iron beds helped to create the ores bodies in the first place (Chapter 1). The first publication on this process appears in Biringuccio’s 1540 text *Pirotechnia* in which finely crushed ore is mixed with table salt (NaCl), vinegar, mercuric chloride (sublimite) and verdigris (copper



**Figure 2.52** The Patio process apparently relies on chloride ions to bring fine silver particles into solution as a soluble silver chloride through an oxidation reduction reaction. The silver is deposited into mercury as an amalgam by a second oxidation reduction process which liberates mercury.



**Figure 2.53.** Ground silver ore, table salt, and mercury is worked on flat surfaces called patios. C. Schnabel and H. Louis, 1905, *Handbook of Metallurgy*, Vol. 1, 766.

toward the mercury drops and form a silver mercury amalgam. Large losses of mercury occurred during this step due to the solubilization of the mercury. The final step was the heating of the amalgam to drive off mercury and recover the silver (Figures 2.52 and 2.53).

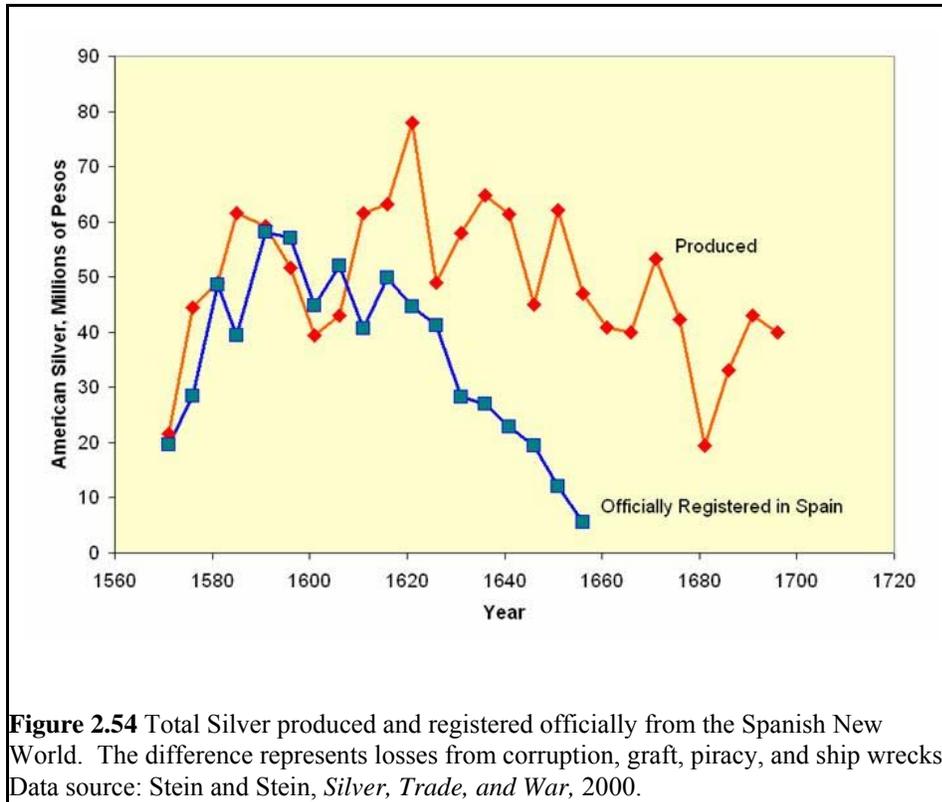
Despite the phenomenal success and importance this amalgamation process played in New World silver mining Medina never was able to profit from it. Patent laws were not much observed, nor did the King of Spain see fit to award him a retirement stipend. The Spanish throne did make a large amount of money from the process, not only by increasing production of silver, but by

owning and taxing mercury production at Huancavelica (Villa Rica de Oropesa de Huancavelica, Peru). Most of the mercury mined in them was used in the Bolivia and Peruvian silver mines because transport costs across the mountains to Mexico was too high. Beginning in 1558 when Philip II ascended the throne the supply of mercury for Mexico derived from Almaden. Philip II instructed the operator of the Almaden mines, Ambrosio Rotulo, to send their entire output to Mexico. As a result, the large silver production in the New World did not result in massive lead pollution like that of the Roman Spanish mines. It did result in widespread mercury contamination. It

acetate).

Medina used chloride salts was used to dissolve silver from various crushed ores, move them

has been estimated that 612 tons/year of mercury were lost from the silver mines between 1580 to 1900 A.D. This amount to 196,000 tons of pollution (Nriagu,



description of working conditions in the 1700s at the Real Del Monte silver/lead mines. A work crew consisted of a pikemen, bearers, and captain. The ore was pried out with crowbars after being blasted with gunpowder *tacos*. Three *peons* or porters carried the ore for pikemen at well manned mines. The porters carried sacks weighing 146 to 196 pounds each up logs hacked into thousands of shallow steps. These steps grew slime and fungus and were inclined at a 45 degree angle. A conventional ladder could not be used because a barefoot man carrying that weight could not support his arches on a ladder rung.

1996).

The increased silver production by the patio process exacerbated rather than solved Spanish financial woes. The total gold and silver in Europe roughly doubled immediately following the New World conquest. Over a 10 year period from 1536 to 1546 imports of silver rose by a factor of 6 (Figure 2.54) (Stein and Stein, 2000). Inflation resulted. It was the highest in Spain (50%) from 1500-1525. Inflation was less further away resulting in importation cheap goods into Spain, contributing to an unfavorable balance of trade. It has been argued that the wealth of the New World channeled through Spain inevitably resulted in Spanish bankruptcy (Aitchison, 1960). The large amount of available money was used to defend Spanish Hapsburg interests in Europe and wage war in the Lowlands. Other money flowed out of Spain to fuel the incipient glass, cloth, and textile industries of Northern Europe ((Stein and Stein, 2000). As a result of the inflation, there was a surge in alchemical literature (see Chapter 6).

Procedures used to work the early Mexican mines do not appear to be greatly different from those used in Greek and Roman times. Following is a

The workday was 12 hours long in shafts with no sanitation. Workers bailed water, constructed scaffolding, or made rope for lifting ore from the main shaft. Women and children sorted sacks of ore, including silver, silver sulfides, black silver, antimony sulfide, lead sulfide, and arsenic sulfide. The lead and galena was smelted. Workers were paid four reales, the equivalent of 50 cents for a twelve hour shift. One real could buy 5 pounds of meat. A house could be purchased for 2,000 reales (Ladd, 1988).

Many laborers were forced to work in the mines. In 1754, Pedro Romero de Terreros became sole owner of a mine and his first act was to petition the King of Spain for permission to force laborers into renovating the mines and increasing his refinery capacity. Neighboring villages were expected to supply work and relief crews for 15 hour shifts a piece. The conscripted Indians complained about the loss of labor necessary to make enough food for paying church tithes. They also protested the occupational hazards associated with mining (lung disease, arsenic poisoning, lead poisoning). Diego Felix said he was forced to tread mercury into mineral mud, which felt cold. He complained that he was not allowed to rest

not even when he was tired. Some workers were beaten to death in stamp mills for failing to complete tasks they did not know how to do. One Creole (mixed Indian/Spaniard) noted that foremen put iron collars on the Indians.

Although forced laborers were supposed to receive 2.5 reales a day, they often were not paid. They were required to work a second 15 hour shift when their relief shift did not come. From their pay, death insurance was subtracted: ½ real for the Mass and ½ real for the coffin. These conditions resulted in the first New World labor strike from Oct 1766 to February 1767.

Although Mexico's silver production was obtained by use of mercury not by lead, the country has suffered from major lead pollution because its lead ores are so abundant. One of the major silver/lead ores was that of Sierra Mojada in Coahuila, found in 1878. This ore produced 20 ounces of silver per ton. The discovery of this metal helped bring about a railway system. Before the railway, only ore of 1kg silver/ton plus 30% lead composition could pay for transportation costs. Robert S. Towne first carried ore to Kansas City by mule for smelting, but then helped open, in 1890, the Mexican Northern Railway connecting Sierra Mojado to El Paso Texas smelters (Bernstein, 1964), p. 21-23. The high-grade Mexican ore prompted American producers to persuade the U.S. Congress in 1890 to pass the McKinley Tariff which imposed a duty on lead imports.

Mexico continues to be a major exporter of lead. In 1979 it and Peru were the leading exporters of lead in Latin America.

### North American Colonial Lead Mines

The first lead mine in what is now the United States came with the founding of the Virginia colony (1607) (McCord), p. 535. John Berkeley, his son, and 20 workers were sent from England to work an iron ore at Falling Creek. A lead body was discovered nearby, but the location was lost soon afterward. The Native Americans apparently knew the ore was valuable to the colonists. Robert Beverly writes in his 1705 "*History and Present State of Virginia*":

*The Superintendent of this Iron-Work had also discover'd a Vein of Lead ore, which he kept private, and made use of it to furnish all the Neighbours with Bullets and Shot. But he being cut off with the rest, and*

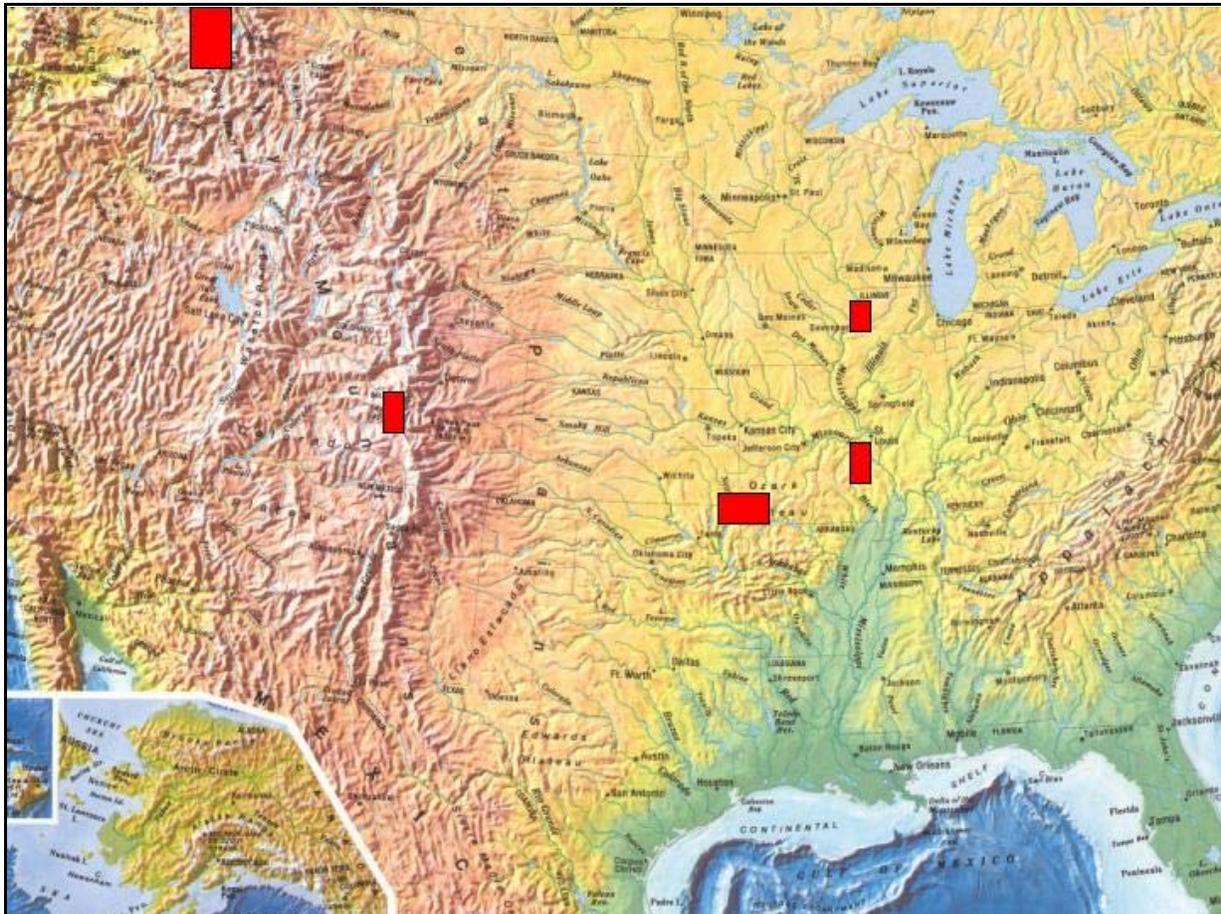
*the Secret not having been communicated, this Lead Mine could never after be found; til Colonel Byrd, some few years ago, prevail'd with an Indian, under Pretence of Hunting, to give him a Sign, by dropping his Tomahawk at the Place (he not daring publickly to discover it, for fear of being murder'd.) The Sign was accordingly given, and the Company at that Time found Several Pieces of good Lead Ore upon the Surface of the Ground, and mark'd the Trees thereabout: Notwithstanding which, I know not by what Witchcraft it happens, but no Mortal to this Day could ever find that Place again, tho' it be upon part of the Colonel's own Possessions. And so it rests, till Time and thicker Settlements discover it.*

Few other mines were operated during the colonial period. A small body was tapped out near Easton, Massachusetts by 1651. In 1750 a new body of lead was found in Dutchess County, N.Y., and in New River, Virginia, 1750. A deposit was developed in Southampton, Ma. in 1765, but discontinued during the Revolution.

The paucity of lead ore mines was a problem during the Revolutionary period. A statue of George III was pulled down in 1770 to create 42,000 bullets. The Colonial Congress imported experts on lead smelting and refining from abroad. Lead was produced in Great Kanawha, Virginia but the operation did not turn out more than 25 tons/lead per year. The exhaustion of lead supplies during the war led to melting down of roofs, gutters, spouts, pewter, organ pipes of old churches, and leaden coats of arms from gravestones.

Graseillier was the first European to mention the lead of Galena, Illinois (Figure 2.55). He describes mines among the Boeuf Sioux in 1658-59 (Schafer, 1932). The main lead bodies lay in the French-controlled Mississippi Valley. Jesuit Father Hennepin's 1687 map locates lead mines near Fever River (Galena, Ill). Nicholas Perrot was given lead in the form of PbS (galena) from a Miami chief in 1690. Perrot established a lead mine on the Mississippi. It used buffalo horns and deer antlers for picks. Crushed rock was carried in birch-bark baskets to a hillside where charcoal was laid over holes. These holes had channels dug at the sides from which the molten lead flowed. The yield was 50%.

Le Sueur, commandant of Chequamegon Bay, discovered lead mines at Lake Pepin. In 1699 he was commissioned by the King of France to work the mines, returning with 30 workers. Philip Renault



**Figure 2.55:** Topographic U.S. map showing location of some important lead mining areas. From left to right: Idaho: Coeur d’Alene; Center left: Leadville, Colorado; Center bottom: Tri-State Mines of Missouri, Oklahoma, and Kansas; Center right: Viburnum Trend of eastern Missouri, Upper Center: Galena of Illinois.

continued the search. In 1720 he traveled from France with 200 workers, purchased 400 slaves in Santo Domingo, and moved to an area near St. Louis to mine what he hoped was lead with silver. The Indians plundered the operation, and he left in 1742.

Mining continued throughout the colonial period. Captain Henry Gordon reported in 1766 that the French had a large lead industry in the area and were transporting twenty tons of lead from Illinois to New Orleans twice a year. Again, Native Americans often put an end to mining. Julien Dubuque (permit 1788) was the most successful, marrying a chief’s daughter. His mine near Dubuque, Iowa, across the Mississippi from Galena, Ill., produced 30,000 ingots of lead annually. It sold for about about 3 cents/lb. He reported to Major Zebulon M. Pike in 1805 that he

made 20 to 40,000 lead pigs a year.

In 1809 Nicholas Boilvin, US agent for the Winnebagoes, reported that the Sauks, Foxes, and Iowas were involved in lead trade, producing 400,000 lbs of lead for exchange Canadians. The first “American” shipment of lead is credited to Colonel George Davenport an agent of the American Fur Company in 1816. The shipment took place despite an 1816 treaty leaving control of the area to the Native Americans. American miners showed up abundantly in 1819. They often married Native American women. Heavy immigration began in 1829. In 1828 the right to the lead district was acquired from the Indians for \$20,000. In 1832 all settlers using a Spanish claim were ejected and the land was resold under American law ((Schafer, 1932; Wright, 1966)).

Galena had about 2,300 lead miners in 1820.

Their ranks swelled to 10,000 within several years. The district began produced 192,000,000 lbs of lead in 1844, making it the lead-producing capital of the world. Over the period 1835-1848, an estimated \$14,178,000 worth of ore was extracted.

The burgeoning population in the area and the large amount of ore for export required necessitated better transportation routes. Shipments occurred via river with a small portage distance northeast across Wisconsin to Green Bay. Overland transport to Milwaukee also occurred. Chicago lobbied heavily for the building of a railroad to connect the lucrative region with its own much ballyhooed Illinois and Michigan Canal linking Lake Michigan with the Illinois River and thus the Mississippi. Despite the enticements of Green Bay, Milwaukee, and Chicago, 95% of exported lead moved the short distance down the Fever River to the Mississippi and from there to New Orleans for shipping up the Atlantic coast.

In order to accommodate the river traffic, the upper Mississippi rapids had to be channeled and a series of locks constructed. The trade to Galena was the major support of the upper Mississippi river boat traffic. In 1823, the first steamboat docked in Galena:

the *Virginia*, captained by John Crawford in 1823 (Petersen, 1930). In 1826, four steamboats were plying the waters to Galena. By 1829, 300 trips were made annually by 30 different boats. Freight costs on these boats were a function of the total lead requiring transport, the number of boats competing for the freight, the river levels, and the season of the year. In 1841 it cost 92 cents to transport 100 pounds of lead.

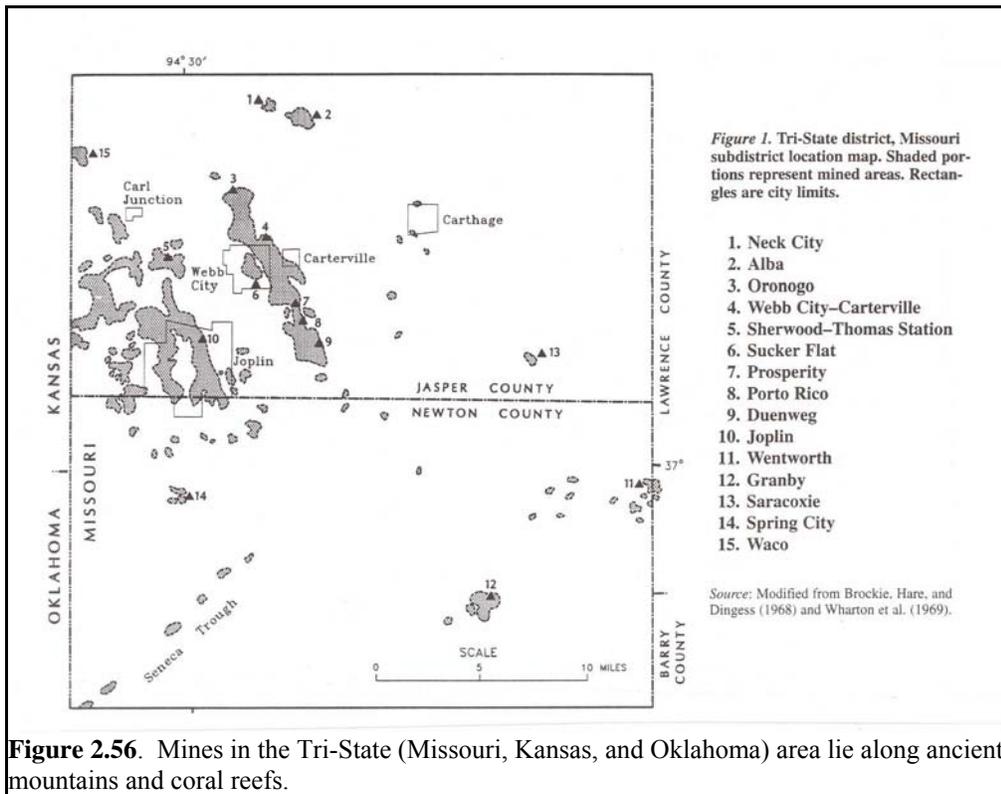
According to Peterson immigration to the United States was shaped by development of the steamboat traffic on the upper Mississippi in response to the transportation requirements of the Galena lead district. Such easy transportation enabled the mid-1890s settlement of Minnesota by northern Europeans.

### MODERN MINES

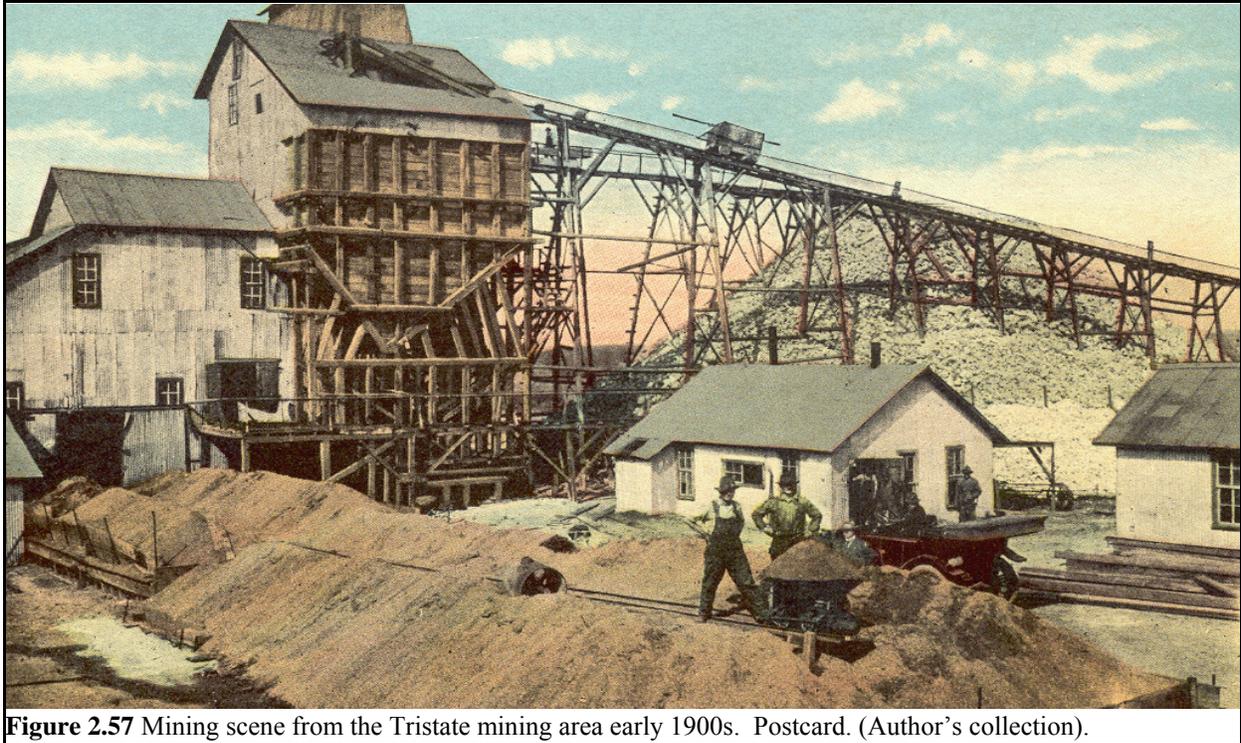
The following section are includes modern commercially important mines. We saw that fuel supplies were a major consideration in earlier mining efforts, as well as technology to deal with water. These two constraints were not as important in the exploitation of modern mines. Labor, however, continued to be a major constraint in mining operations.

### Tri-State Mines and Viburnum Trend U.S.A.

The Tri-State Mines (Missouri, Oklahoma, Kansas) went into production in the mid-nineteenth century (Figure



**Figure 2.56.** Mines in the Tri-State (Missouri, Kansas, and Oklahoma) area lie along ancient mountains and coral reefs.



**Figure 2.57** Mining scene from the Tristate mining area early 1900s. Postcard. (Author's collection).

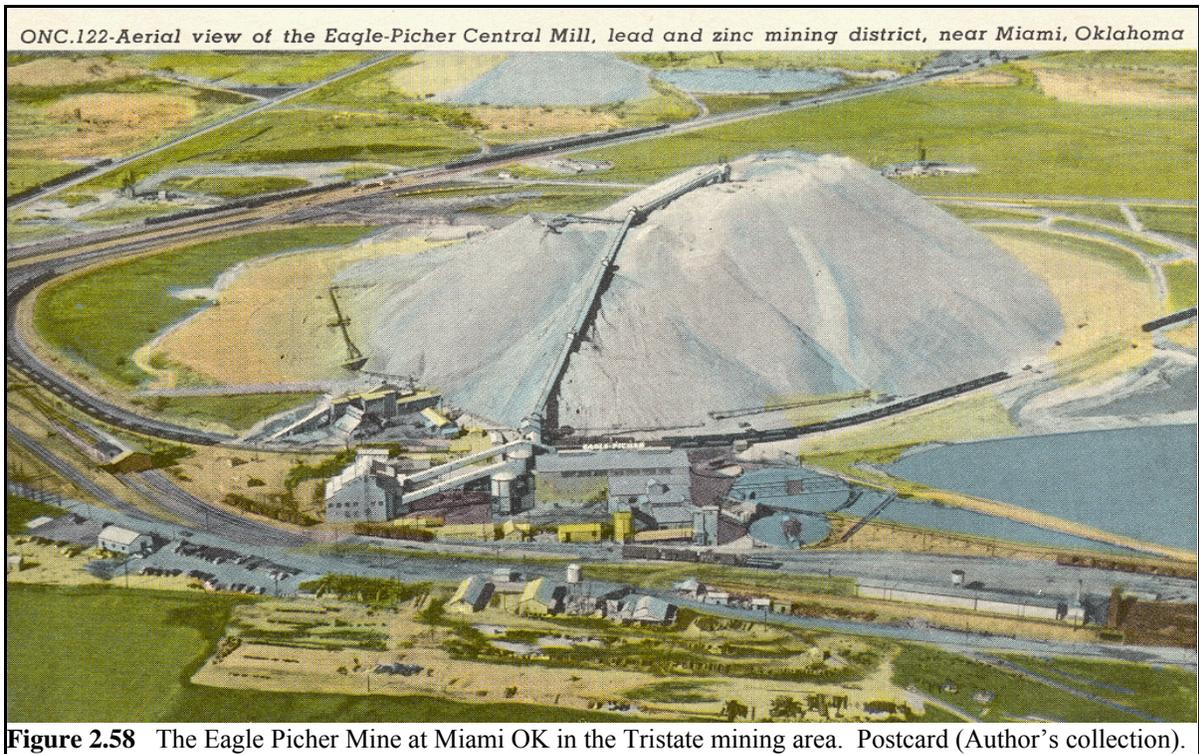
2.56-58). These ores are part of an ancient collapsed volcanic dome of Pre-Cambrian origin. As with any other ore bodies, dissolved carbonate rocks created a porous matrix suitable for deposition of further minerals. Dolomites may be residues of earlier reefs, with mineralization occurring along fraction zones of the early reef structure. The time sequence appears to be dolomite deposition, followed by sphalerite ( $ZnS$ ) at  $135\text{ }^{\circ}C$ , then placement of galena, followed by chalcopyrite ( $CuFeS$ ), marcasite ( $FeS_2$ , orthorhombic), pyrite ( $FeS_2$ , cubic), then calcite ( $CaCO_3$ ) and barite ( $BaSO_4$ ) at about  $25\text{ }^{\circ}C$ .

The western Missouri ore was discovered noted by Henry Rowe Schoolcraft in 1818 who easily manufactured bullets from the ore, implying that the ore was exceptionally pure. It was reputed so pure that the Oronogo lead could be directly melted in a wood chip fire ((Gibson, 1972). Schoolcraft describes a simple process of ore purification used by the Indians in the area as a pit dug into the side of a hill four feet wide with three foot side walls in which logs were laid. The ore was placed over the logs and then covered with brush and set on fire. The lead metal melted through to the bottom and ran down the side of the hill where it was collected (Gibson, 1972).

The first European permanent settlement of

the Tri-State area was in 1833 by farmers. The first farmer who became a part-time miner was in 1848 at which time prospecting began in earnest. A smelter was constructed in 1849. By 1856 large furnaces that could output 12 million lbs lead/year were built. The mines ceased production temporarily during the Civil War but moved into a "boom" period during the 1870s (Lasmanis, 1997). Up until 1865 the mines were shallow as the ore was very pure and abundant at the surface which made digging below the water line (~60 feet) less desirable. The ore also changed composition toward a more zinc rich material.

In 1872 miners were leasing land from farmers and paying 10% royalty on the profits. Shortly thereafter companies began forming which leased large contiguous segments of land for the 10% royalty in order to control an entire vein. These rights to mine were subleased to miners who still remained the main risk holders, supplying all the labor and equipment. About 1865 the companies went into the business of also buying ore and began requiring that the miners subleasing sell their ore to the company smelter. With the larger amount of capital available to the companies they began paying for the sinking of exploratory shafts at \$100-150 a shaft. Once a site was proven to contain valuable ore miners were charged a second fee in



addition to the royalty. The charging of such fees lead to a 3 day riot in 1874 in Joplin, Mo., which resulted in the burning of the Picher Lead Co. smelter. Royalties were reduced.

Before 1900, several hundred different mines were owned by dozens of different operators. The mines were often only 100 ft apart. They were worked by two-man teams using picks, shovels, and a horse or windlass to hoist the ore cans to the surface. One worker picked, shoveled and loaded, while the other hauled. Payment was by the can. Thus the workers had no incentive for wet-spraying the mine to reduce the dust hazard. A typical shoveler filled 60 to 90 cans of ore during an 8 hour day. A single man lifted 75,000 to 100,000 pounds per day, well over the industry average at the time of 32,000 to 38,000 lbs. Each can was worth 5 to 8 cents, meaning that each piecemeal work yielded \$4-5 day.

Mining activity grew because of WWI demand. Mining became more efficient with the use of drillers and blasters. The increased efficiency meant increased rates of lung disease (silicosis) and associated with it tuberculosis. Between 1905 and 1929 lead production rose from 388,000 to over 650,000 tons. The newer mines were deeper and more amenable to mechanization, allowing consolidation of producers to

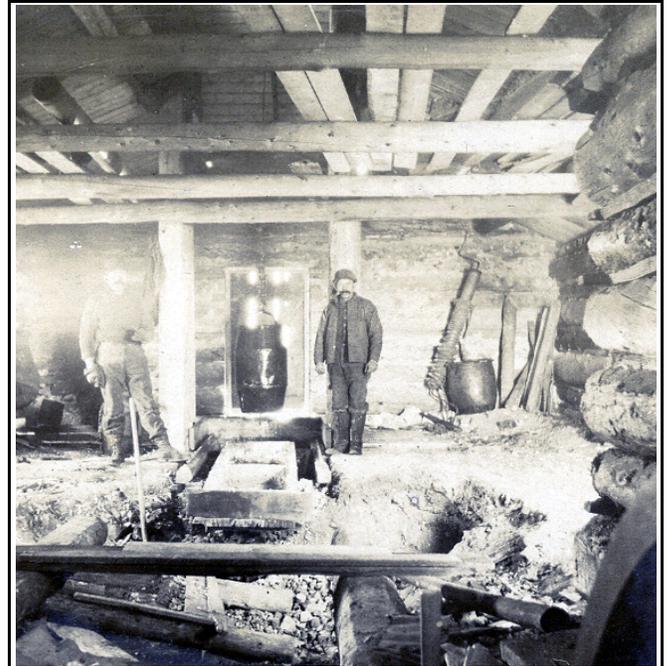
occur by the mid-1920s. The consolidation was also driven by the expansion of lead produced in western U.S. Between 1919 and 1939, the tonnage of production stayed constant, but the dollar amount dropped in relation to the western mines. In 1919, the total value of zinc and lead shipments in the nation was \$75.5 million. The states of Kansas, Missouri, and Oklahoma accounted for 61% of this figure. This percentage dropped to 45% by 1929, and to 28% by 1954 (Markowitz and Rosner, 1990).

The introduction of power drills and high-intensity explosives caused a large increase in health problems. One owner employed 750 men between 1907 and 1914. By 1916, "only about 50 of these were still living, and all the others except not more than a dozen were said to have died from tuberculosis." In 1906, the miners gained representation from the militant Western Federation of Miners, an affiliate of Industrial Workers of the World. The primary goal of the union was to see health insurance added to the workers pay.

The Viburnum Trend ore body (see Chapter 1) was found in 1948. Between 1971 and 1974 the Buick Mine ranked as the largest lead producer in the United States and the second largest zinc producer in the world. From 1960 to 1994, a total of 11,349,013 short-tons worth \$6,401,938,497 was extracted, while \$1,232,682,208 worth of zinc was extracted. 45,897,555 troy oz. of silver worth \$281,591,665 were also extracted as well as 361,800 short tons of copper.

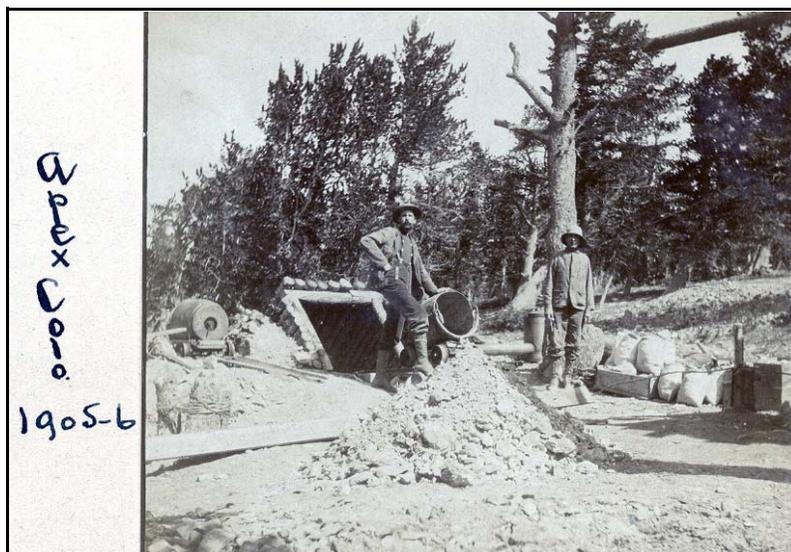
The dust from the trucked metal in the vicinity of the mines at Herculaneum, Mo. has been measured at 300,000 ppm meaning that the dust content is 30% lead. Doe Run purchased 60 homes in the town between 1990 and 2000 in order to deal with the lead content. Residents in 2002 pressured the U.S. government to also begin buying out residents as 24% of the children were found to have elevated blood lead levels (Strange, 2002).

The amount of lead in the runoff water in the Tri-State area depends upon the presence of iron, just as we noted for Rio Tinto run off. The reaction driving the solubility of the solid lead sulfide is the oxidation of sulfide to sulfate when iron, as the cation  $Fe^{3+}$ , accepts electrons to form  $Fe^{2+}$ .



**Figure 2.60.** Inside the mine shelter where the hoist was located. Stewart Zwingli Schenck 1907 silver prospecting. Photo Schenck. (Author's Great-Grandfather).

### Leadville, Colorado, USA



**Figure 2.59.** Schenck's Apex, Co. Mine. After failing at prospecting, Schenck left his wife. Family rumor says with a dance hall girl. He eventually ended up owning a parking garage in Chicago. (Author's Great-Grandfather's photo album).

The next major impact of U. S. lead mining was associated with western gold and silver mines that were mostly based on cerussite ore,  $PbCO_3$ . These mines offered rationale for western exploration. While lead was indeed produced in Leadville, it was most notable for its gold and silver mines. The mines in Utah and northern Idaho were commercially significant lead producers during the early 1900s (Figure 2.45).

The mine at Leadville, Colorado brought that state into the Union (Voynick, 1984). The silver mine was owned by Tabor, who moved from the East Coast to try his fortune. He failed at homesteading in Kansas and moved on to Colorado where he operated a dry goods store. After lending seed money to some miners, he became owner of the Matchless mine. He shed his wife, became a United States Senator, and married a young divorcee, Baby Doe. Their marriage



**Figure 2.61** Leadville miners' cabins were small to keep out the cold of mountain winters: Stephen M. Voynick, *A Miner's Epic*, Photo: Colorado Historical Society.

announcements were printed on silver and they lived in Denver hotels at the cost of \$10,000 a week during the 1890s (Coquoz, 1964). With the collapse of the silver value (Silver Panic of 1893), he became destitute, but advised Baby Doe to hold on anyway. She lived out

the rest of her life as a "bag lady" in an unheated cabin next to the silver mine, inspiring the opera "The Ballad of Baby Doe".

Also from Leadville was Molly Brown, wife of John Brown, the owner of the Little Johnny silver mine. Molly Brown, an uneducated Irish immigrant, wished above all else to be accepted by Denver high society. After being rebuffed she took the Continental tour to acquire antiques, polish, and sophistication. She return on the Titanic. When asked by reporters in New York if she had feared for her life, she replied that she was unsinkable leading to her name (and the musical) "The Unsinkable Molly Brown."

It is suggested that about 9,000 western lead/silver miners were poisoned by lead. This number is high because many western ores had a cerrusite, as opposed to galena, form (Table 2.3) (McCord). Another prevalent disease was pulmonosis, which was related to intake of activated silica (ground- or sand-blasted). The legal

standard for the time stipulated that workers recognize the hazards of the job and accept the risks by accepting the job. They were free to leave at any time. All medical care costs were to be assumed by the miner out of his \$3/day wage for a 10-/12 hours of work (Voynick, 1984). This should be put in context of the Leadville mines in which, over the course of 20 years, \$250,000,000 of gold and silver were extracted.

Leadville was initially founded as a gold prospecting town during Pike's Peak Gold Rush of 1861, the event which led to the formation of the Colorado Territory. In 1874, a particularly rich vein of lead carbonate bearing 20-40 ounces of Ag/ton was discovered. This new vein required industrialization (train services, hydraulics for water washing). The lead could be sold at 6 cents/lb and the silver for \$1.16/ounce meaning it was particularly profitable. In 1877, another vein was discovered containing 50% lead and >200 ounces Ag.

**Bunker Hill Mines, Coeur d'Alene, U.S.A.**

The mines at Coeur d'Alene, in the upper Idaho and Montana region also played an important political role in

**Table 2.3: Lead Poisoning From U.S. Western Mines**  
source: McCord, C. P.

| <u>Mine</u> | <u>Period</u> | <u>Hospital Admissions for lead</u> |
|-------------|---------------|-------------------------------------|
|             |               | (Estimated 10% of victims)          |
| Jordan      | 1875-1898     | 67                                  |
| Spanish     | 1875-1898     | 69                                  |
| Yosemite    | 1875-1899     | 69                                  |
| Telegraph   | 1876-1898     | 205                                 |
| Lead Mine   | 1877-1895     | 88                                  |
| Brooklyn    | 1884-1892     | 249                                 |
| Mayflower   | 1890-1892     | 63                                  |
| Dalton      | 1893-1897     | 50                                  |
| Total       |               | 870 = 8700 victims                  |



**Figure 2.62.** Bunker Hill Zinc electrolytic plating plant. Postcard. (Author).

American history (Figure 2.55, 2.62, 2.63). These mines, like Leadville's, were originally exploited for their silver, but were also high in lead, and became major lead production centers.

The mining history of the western United States begins with the 1849 California Gold Rush. Placer (nugget-sized) gold declined by 1855 and mining activities moved to Nevada, Colorado, Arizona, and Idaho. The Colorado gold rush at Pike's Peak began in 1859 (Cripple Creek), with an excursion into the Comstock Lode, Nevada and Montana, and back to Leadville, Colorado.

The Virginia City, Nevada rush occurred between 1863 and 1864. It was followed by the Butte, Montana rush of in 1864. The gold placer rush crested in 1866-1870, and the Anaconda mines opened in 1872-1884. Eventually, the heyday of prospecting ended, and large scale mines were established based on silver/lead/zinc ore bodies.

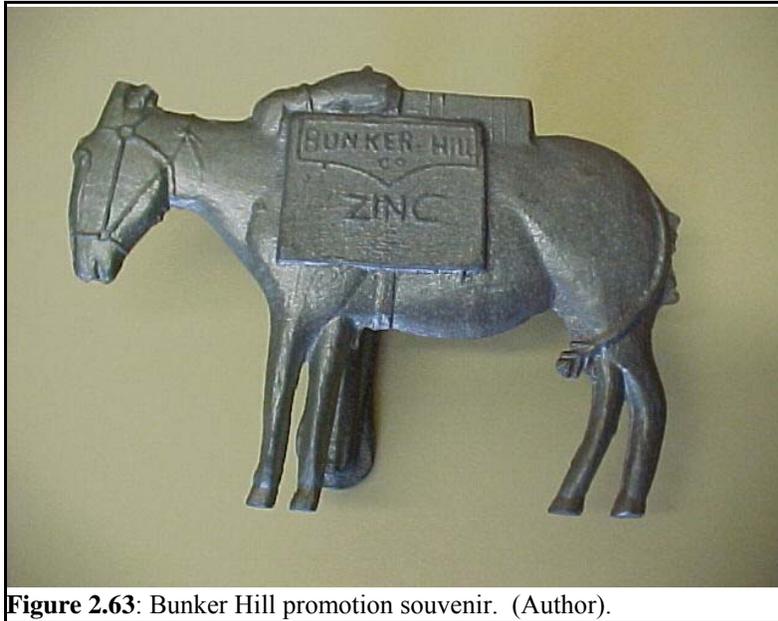
The mines in the Coeur d'Alene area (upper Idaho and Montana) play a unique role in western U.S. history. In this region labor successfully exercised its muscle. An international union movement, International Workers of the World first arose here. The union movement was focused upon wages and

health premiums, benefits demanded because of conditions within the silver lead mines. Other major labor issues included decreased wages due to a devaluation of silver and increased labor resulting from immigration.

In order to understand the devaluation of silver, we need to examine the politics of American coinage. Originally, American coinage was based on English, Spanish, and French gold and silver coins. Bimetallism was favored. In bimetallism the relative worth of silver to gold is fixed at some ratio, often a 16:1 ratio that makes gold more valuable (Laughlin, 1901).

Although the early American Republic began with Jefferson-inspired paper currency, by 1785 public demand pushed the monetary system back to metal. Because of a lack of gold, silver became the monetary standard. A double standard (bimetallism) of both gold and silver was advocated by Alexander Hamilton. He felt that gold's "real" value would fluctuate less than that of any other metal

*As long as gold, either from its intrinsic superiority as a metal, from its rarity, or from the prejudices of mankind, retains so considerable a pre-eminence in*



**Figure 2.63:** Bunker Hill promotion souvenir. (Author).

*value over silver as it has hitherto had, a natural consequence of this seems to be that its condition will be more stationary. The revolutions, therefore, which may take place in the comparative value of gold and silver will be changes in the state of the latter rather than in that of the former.*

The western gold rushes changed the relative value of gold and silver and necessitated that one of these two metals be chosen as the single standard. By fixing the ratio of silver arbitrarily to the floating market value of gold, a default monometallism was created in 1853. This defacto standard was formalized on Feb 12, 1873 when the silver dollar was officially demonetized.

The devaluation of silver had repercussions for the lead mining industry. Much of the impetus for lead mining came from the value of the silver that could be extracted. The devaluation of silver partly contributed to the growth of labor unrest in the mines and elsewhere during that period.

A second cause of labor unrest pertained to immigration. Many of the miners were Irish Catholic. The California Gold Rush of 1849 coincided with the Irish Potato Famine and brought large numbers of Irish to the west of the U.S. A second immigration wave brought more workers to the American west. Out of the 2700 workers at the Comstock Mines during 1880 foreign-born labor dominated. Only 770 were native-born. By 1891, the district employed more than 1200

miners, most of whom were unmarried immigrants from Ireland, Germany, Sweden, Italy, and elsewhere (Derickson, 1988), p. 87.

The Irish miners of the west fell into five classes: those with an Irish background in mining (West Cork men from the copper mines of Hungry Hill), landless farm laborers from Ireland; Irishmen from England's industrial towns; men from the industrial east of the U.S.; and men from other mines in the western U.S. (Emmons, 1990), p. 16. Emmons' study of Butte, Montana, suggests that these Irish were disposed by their history toward communal organizations organized against landlords during the Famine and this history served as the basis for union formation in the U.S. west. A similar assertion is made by other historians (Elliott, 1973). The Comstock miners

were the first to unionize. They requested \$4/day when the owners wanted to reduce wages to \$3.50 in 1864.

Bradley, the manager of Bunker Hill, a major silver/lead mine in Helena, Montana attempted to break the union there in 1894. He deemed his mission to be the "weeding out" of Irish miners and substituting them with "American" workers (Aiken, 1993). Bradley suggested to the home office that unless Irish Catholics "officered, manned, and managed" every aspect of the Bunker Hill operations even complete surrender to union demands would be useless. In response to labor unrest in the face of wage cuts below \$3 a day, management allied itself with the American Protective Association (APA) an anti-Catholic league and a "secret society for the preservation of law and order". Eventually the management convinced the governor to send state troops to the area. The martial law that followed was used to remove Populist elected officials from office.

As mentioned, the labor movement was also

concerned with health. The Western Federation of Miners became militant partly because of experiences with mutual assistance groups in the area of health (Derickson, 1988), p. xiii. The organizers felt that a

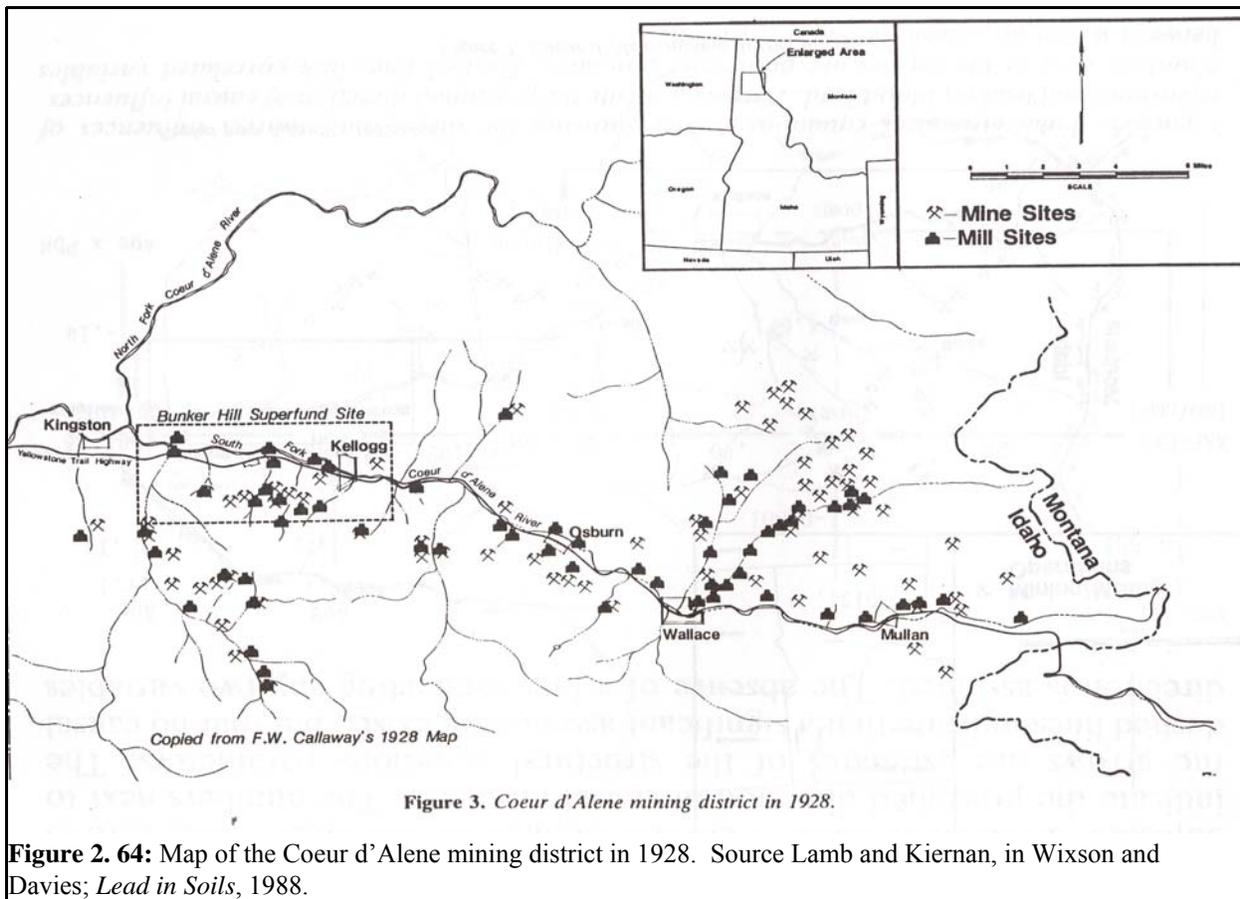
proactive response to health issues would position the unions better politically than would a single-issue focus on wage cuts (Derickson, 1988), p11.

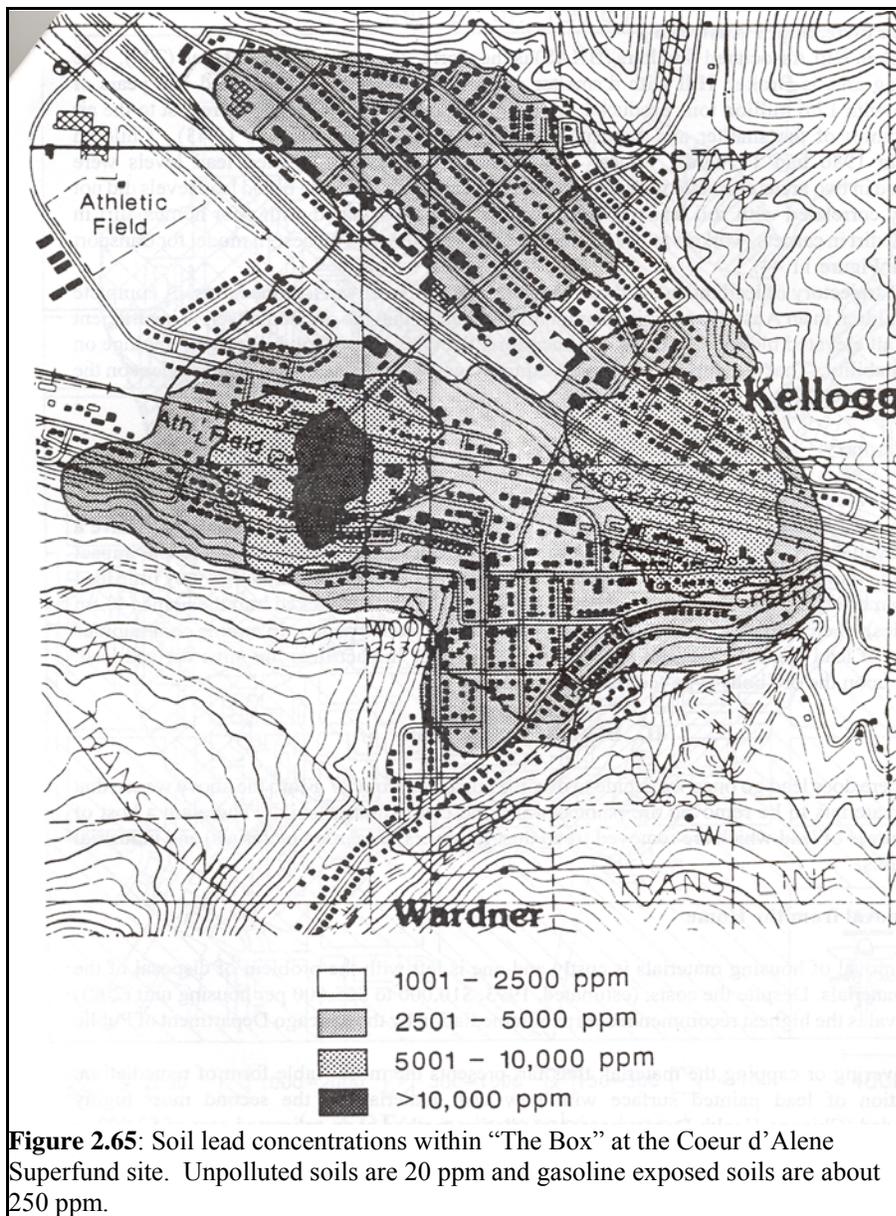
The tensions at the Coeur d'Alene Mines led to the "Mining War" of 1892. The militant union took over the mines (with loss of life) (Smith, 1961). "Big Bill" Haywood, a radical organizer, led the Western Federation of Miners in the 1890s. He established a tradition of radicalism that survived until the 1960s (Aiken, 1993; Malone, 1981).

By 1889 Shoshone County was the third leading lead-producing county in the United States (Figure 2.49). The value of all ore extracted there in 1890 was \$10 million. The production tripled when the mine was consolidated into the Bunker Hill and Sullivan Mining and Concentrating Company.

The typical practice for the mines was to top dump the debris. The debris, in conjunction with deforestation around the site, eventually made its way into the waterways. Shortly after the turn of the last

| <u>Year</u> | <u>#children</u> | <u>mean ug/dL</u> |
|-------------|------------------|-------------------|
| 1974        | 201              | 65                |
| 1975        | 107              | 47                |
| 1976        | 24               | 40                |
| 1977        | 34               | 38                |
| 1978        | 31               | 41                |
| 1979        | 27               | 48                |
| 1980        | 93               | 31                |
| 1981        | 74               | 29                |
| 1982        | 67               | 23                |
| 1983        | 43               | 21                |





the 9<sup>th</sup> U. S. Circuit court of Appeals which said mining companies could not inflict “unlimited injury” on others (Steele, 2002). By 1920 records showed that fish and vegetation in the area was dead. Fine mine sediments from the flotation process called “mine slimes” spread downstream to Lake Coeur d’Alene and the Spokane River. In 1932 the Department of Interior reported that mine slimes had washed down to Greenacres in the Spokane Valley and recommended that mine wastes be placed in settling ponds. In response the Mine Owners Association in 1934 build a dredge at the town of Cataldo to remove 500 tons of mine sediments a day from the Coeur d’Alene river. The tailings were deposited on Cataldo flats. Migrating tundra swans who pass through the Cataldo marshes die at the rate of 5% of the migrating population from lead poisoning (Seattle Spokesman, Karen Dorn Steele, April 14, 2003). Movement was afoot to curtail some of the processes associated with mining, however the onset of World War II interrupted those plans. U.S. troops were sent in to speed up production for

the war effort.

century farmers along the South Fork of the Coeur d’Alene River sued over “leaded waters” they claimed were killing their crops and animals. Given the reluctance of the government at the time to place any restrictions on economic activity the lawsuit was unsuccessful.

In 1912 Bunker Hill introduced a new process to extract more metals, a flotation process. This process involved greater use and pollution of the watershed. In 1917 Cataldo farmer Jacob Polack’s lawsuit against three mining companies was upheld by

the war effort.

Debris from mining continued to be dumped directly into the river until 1968. Of that debris and estimated 72 millions tons moved to settle at the bottom of the Coeur d’Alene lake and moved on to the Spokane River. An estimated 0.5 million pounds of lead per year moves into the Lake (Seattle Spokesman, Karen Dorn Steele, April 29, 2003) and of that 24,000 pounds move into the Spokane River per year. Other debris was deposited directly into slag heaps in the vicinity of the smelter. The debris is estimated to cover

a football field 4 miles high. The most contaminated area is known as “The Box” a 21 mile Superfund site running through the town (Figure 2.64). Within “The Box” are several mills and a smelter built in 1917 (Lamb and Kiernan, 1993). It operated at a capacity of 300 tons of metallic lead per day. Soil lead contamination in the town ranges from 626 ppm to 18,600 ppm. Mean soil lead concentrations at Smeltonville at 5502 ppm (Figure 2.65). At Kellogg it is 3682 ppm. Contamination along the rail route which shipped ores to the Tacoma, Wa., Refinery is also extremely high.

This is a superfund site. The first mill for processing village was studied extensively 1974, 1975, 1983, and the blood lead survey is given in Table 2.4. The study concluded that soil and dust have an independent contribution to blood lead levels.

Over the entire period of operation the mines were estimated to have removed \$5 billion dollars of material.

### Broken Hill, Australia

The history of the Broken Hill lead mine in Australia (Figure 2.66) is also one of labor involving the Amalgamated Miners’ Association (Barker, 1996). The Amalgamated Miners’ Association was created in 1874 in response to company policies that forced wage cuts and increased working hours.

The Broken Hill lead mine history begins in 1883. On September 5, boundary rider Charles Rasp registered the first mineral claim on what is now called. By June 20, 1885 a first prospectus of the Broken Hill Proprietary Co Ltd (BHP) had been issued. Two months later the first stock was issued. A train linked Broken Hill to Adelaide by 1888. Four years later, in 1892, the first set of strikes began when the miners received the following letter from the mine administrator (Ebbels, 1965), p. 141-145:

*Melbourne, June 30, 1892*  
*R. Sleath, Esq.*

1. *As our communications of the 0th and 17th June do not appear to have received adequate consideration at the hands of your executive, after careful deliberation we are of opinion that from the tenor of your correspondence no good results are likely to arrived at by its continuing.*

2. *The companies have therefore decided*



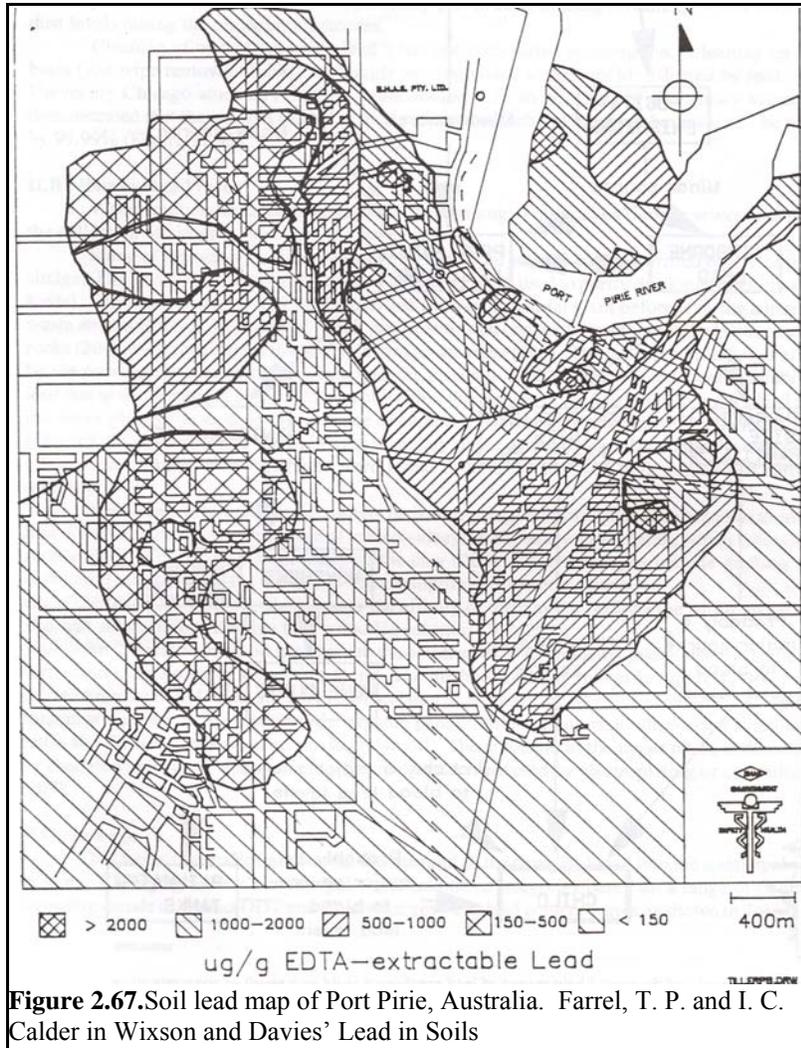
**Figure 2.66** Broken Hill Mines of Australia are located to the northeast of Adelaide.

*unanimously to give your Association notice that all agreements existing as between the said companies and the A.M.A. will terminate on and after Saturday, July 30th, next.*

3. *The stoping will in future be carried out as the nature of the ground may require: (a) prices to be fixed by the manager; (b) payment by results for specific work; and (c) by open tender.*

4. *The directors wish it to be distinctly understood that they do not intend to interfere with the rate of wages at present being paid for overground or underground work, to men working on day wages. But they require absolute freedom to stope on contract.*

The term “stope on contract” means the ability to hire non-union workers at wages negotiated between the administration and the individual laborer. The miners responded immediately, with a strike on July 4, 1892. In their words:



**Figure 2.67.** Soil lead map of Port Pirie, Australia. Farrel, T. P. and I. C. Calder in Wixson and Davies' Lead in Soils

*We were told with shameless hypocrisy that there was no desire to cut wages. How does this accord with the crude yet comprehensive words of the clause, "By open Tender"? Given an overplus of labor, and men will fight for work to sustain a rate unheard of on the Barrier. Necessity knows no law, and harpies are ever ready to fatten on the poor, starving wretches who through deep-seated evils which affect society, must die or sell the brief remnant of their strength for what the taskmasters choose to offer it.*

*Was it for this that hundreds of thousands of public money was spent to "import" population? Better, we say, have Australia a howling wilderness rather than that her sons should be compelled to sell themselves*

*into a bondage worse than death.*

On Sep. 10, 1892, rioting took place in Broken Hill over the arrival of non-union labor to work in the mines. Strike leaders were arrested by police with fixed bayonets. Further arrests made in Sydney. In October of that year six Broken Hill union leaders were sentenced to jail terms varying from three months to two years for conspiring to prevent non-union labor from working in the mines. The strike was broken and the miners returned to work.

Another strike resulted from BHP's 12.5% wage cut in 1908. This time, although police clashed with the miners and labor leaders were arrested and charged with sedition, the workers were awarded their previous wages.

At the end of WWI, Australian Prime Minister wanted to ensure imperial control over base metal industry. He therefore arranged for the British government to purchase all exportable Broken Hill surpluses until 1930. In the 1930 the only Australian industrial interest of world significance was BHP. Although BHP lost its monopoly in the 1960s it continues to be a major economic force in Australia. It has stratified into energy production (Powell, 1988).

### **Port Pirie, South Australia: Soil Lead**

The ore of Broken Hill was processed at the Port Pirie smelter. It has had 100 years of production with 12.6 million tons produced. An estimated 160,000 tons of lead were lost to the air from the fumes of the smelter and deposited in the surrounding soil (Figure 2.67). Children surveyed in 1986 had 17 ug/dL values. While the children with elevated lead levels were concentrated in two areas correlate with highest soil lead contamination, the blood lead levels did not statistically correlated with soil lead. A better correlation was obtained with poor homes, dirt in garden soil, dirt in carpets, workers at BHAS, high mouthing activity (Gulson et al., 1996; Gulson et al., 1994a; Gulson et al., 1994b).

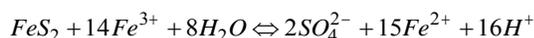
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## Part II: Electrum, Amalgams, Archaeological Evidence, Dispersion, and Modern Metallurgy

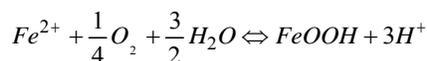
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### Solubility of Release of Metals in Mining

We saw that the Romans mined to the pyrite layer at Rio Tinto and that the resulting waters flowing from in the Rio Tinto (“Colored Water”) were high in copper. The presence of iron serves as a powerful mediating chemical in the solubility of metal minerals. Aquated iron serves as an electron transfer reagent which controls the chemical species of sulfur either as sulfide or sulfate and controls the acidity of the environment which also has a powerful effect on solubility:



The divalent iron can be recycled back to oxidized iron either by oxygen:



also increasing the acidity of the matrix (Carroll et al., 1998), or by microbial action. The later process occurs naturally under many extreme conditions and has been harnessed in biomining (Rawlings, 1997).

### Electrum and Amalgams

Figure 2.2 indicates that gold and silver could be found as very small nuggets. All of the gold nuggets were smaller than the minimum useful size for hammering while some silver nuggets were large enough to be shaped. Both gold and silver can be found in other compounds such as electrum (elektrum) a mixture or alloy of gold with >40% silver. Over all mixtures of gold and silver a solid solution of a face centered cubic alpha phase is formed.

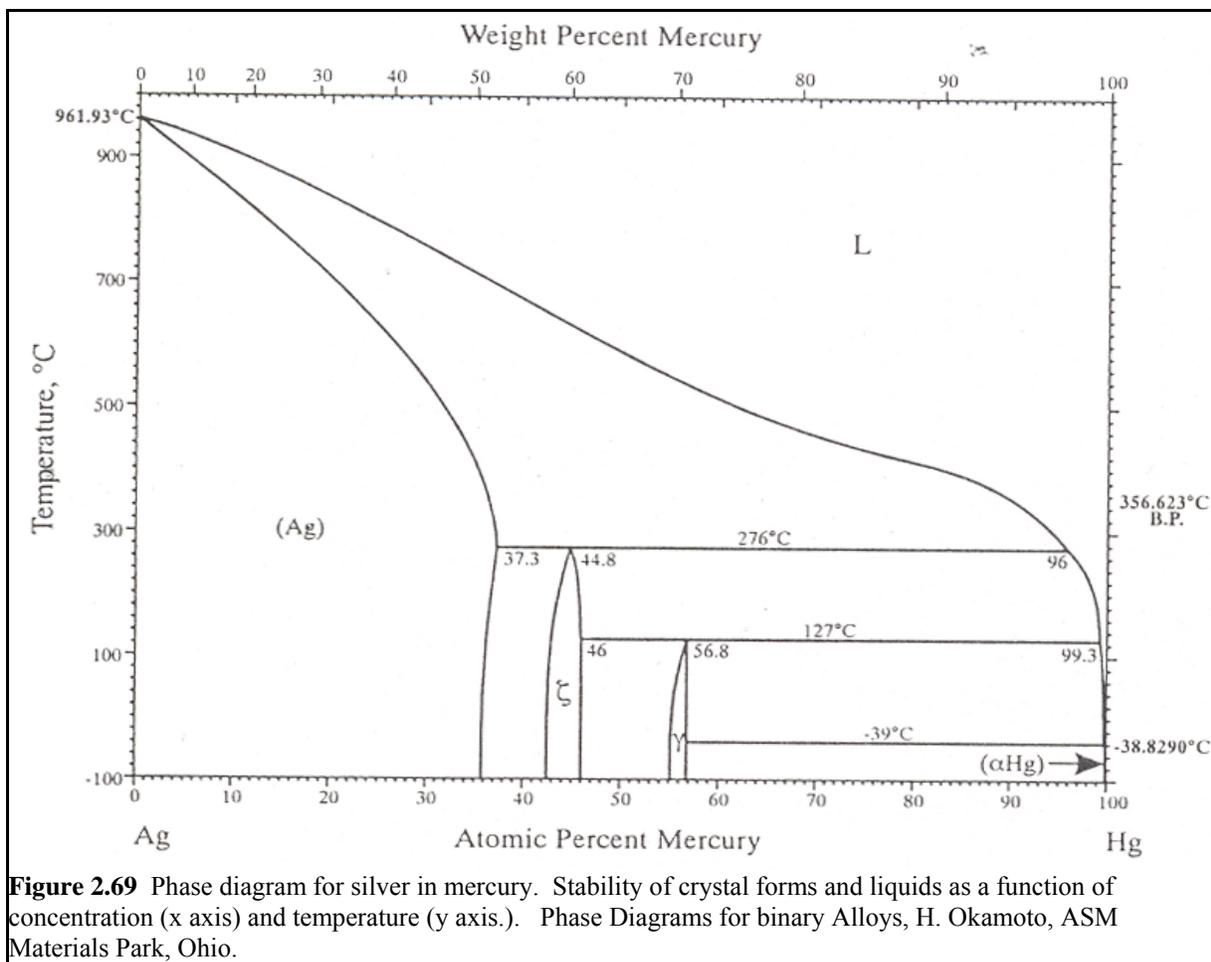
Gold and silver can also be naturally found in minute quantities as amalgams with mercury.

Elektrum (Figure 2.68), gold with >20% silver, was mined in Lydia and used for coinage. By the time of King Croesus the silver and gold were separated. Gold is separated from silver by *parting* of gold and silver by cementation with acidic salts (Ramage and Craddock, 2000) (p. 11). The gold/silver alloy is finely divided and mixed with *cement* (sodium chloride and, occasionally, with alum, ferric sulfate,

and potassium nitrate as active agents) in a *parting vessel* (porous and heat resistant ceramic container). Under heat (>650 °C) the vapor of ferric chloride and chlorine reacted with the electrum along grain boundaries. Silver was corroded to silver chloride which volatilized and was removed from the gold into the porous ceramic container, from which it could be recovered by cupellation. The cementation parting process remains of Lydia have been excavated at Sardis and are consistent in dating with the rule of King Croesus (561-547 B.C.)

The amalgamation process of purifying silver is related chemically to the natural occurrence of silver and gold mercury alloys (amalgam). The naturally occurring alloy of gold/silver still is of interest in mining operations. As an example most of what is called “placer” gold found in New Zealand derived from mineralized quartz veins was found as a Au/Ag alloy with <10% Ag (Williams, 1974). The quartz was mineralized from Otago schist during Mesozoic collision of volcanic derives and quartz derived materials. Following mineralization secondary processes (erosion and redeposition occurred). Alloys of Au-Ag and Au-Ag-Hg were found in both types of materials (Youngson et al., 2002). Hydrothermal deposits are general face centered cubic structure which materials of secondary origin are formed by reaction between gold and liquid mercury in the near-surface environment. Such reactions take place in a more mercury rich phase and has results in Au-Ag-Hg alloy of hexagonal structure.

When liquid mercury and metals are mixed solid state diffusion of the metals occur and the metal enters mercury up to its solubility limit. More of the metal can be added to the mercury phase pressure, but the result of such an increase in the metal is the formation and precipitation of an intermetallic compound of the metal and mercury. Figure 2.68 shows a *phase* diagram of mercury with silver (Okamoto, 1995). Moving from left to right along the x axis the mixture goes from 100% silver to 100% mercury. Along the y axis is the plotted the temperature at which a transition in the metal compound occurs or at which there is a phase change from solid to liquid. Pure mercury is liquid at room temperature. If a line is traced from right to left at



room temperature (~25 °C) an increase in silver (decrease in mercury) results in the formation of first a  $\gamma$  gamma phase and then a  $\zeta$  solid phase and finally a pure silver solid phase. Figure 2.40 illustrated the patio process in which either horses or humans stamp on a mud mixture of mercury and the finely ground ore to force silver into the mercury. The solid silver rich amalgam is then collected and the silver recovered by heating which decomposes the compound the volatilizes the mercury.

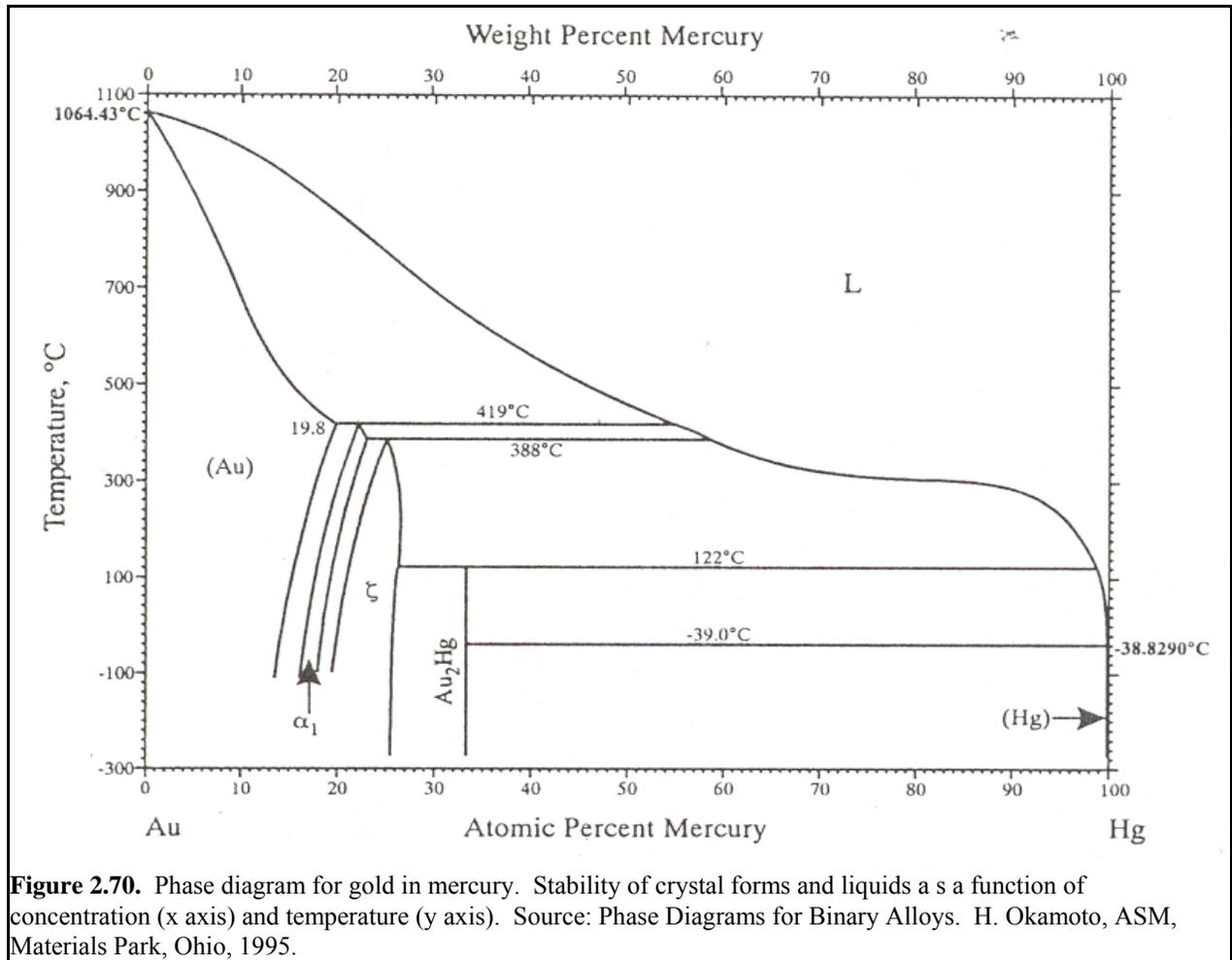
Dental amalgams make their entrance into technology around 1826 when it was found that the change in phase the occurs by forcing silver into mercury results in an expansion of the crystal lattice, i.e. the material expands upon compression (Goldwater, 1972). Dental amalgams consists of 48 to 53% mercury with additions of silver and tin. Addition of mercury to the silver and tin forms the intermetallic phases  $\gamma_1$   $\text{Ag}_2\text{Hg}_3$  and  $\gamma_2$   $\text{Sn}_7\text{Hg}$ . Upon formation of these phases the melting point increases, i.e. the

solution solidifies.

Gold mercury amalgams were extensively used for gilding of surfaces. Like silver, gold forms a number of intermetallic minerals with mercury which retain a gold color and which have altered plasticity suitable for “painting”. One begins by grinding mercury with gold (heating directly will result in loss of mercury by volatilization). The mixture is heated to the boiling point of mercury (357 °C) at which point additional gold can be added to the mixtures (see Figure 2.70). The amalgam is then cooled. A slow cooling results in the formation of  $\beta$  phase of the amalgam which transforms to the intermetallic  $\text{Au}_2\text{Hg}_3$ . If the solution is trapped within the  $\beta$  phase the final amalgam is pale yellow and spreadable.

#### Archeological Evidence of Lead Mining

We do not have to rely only upon written and



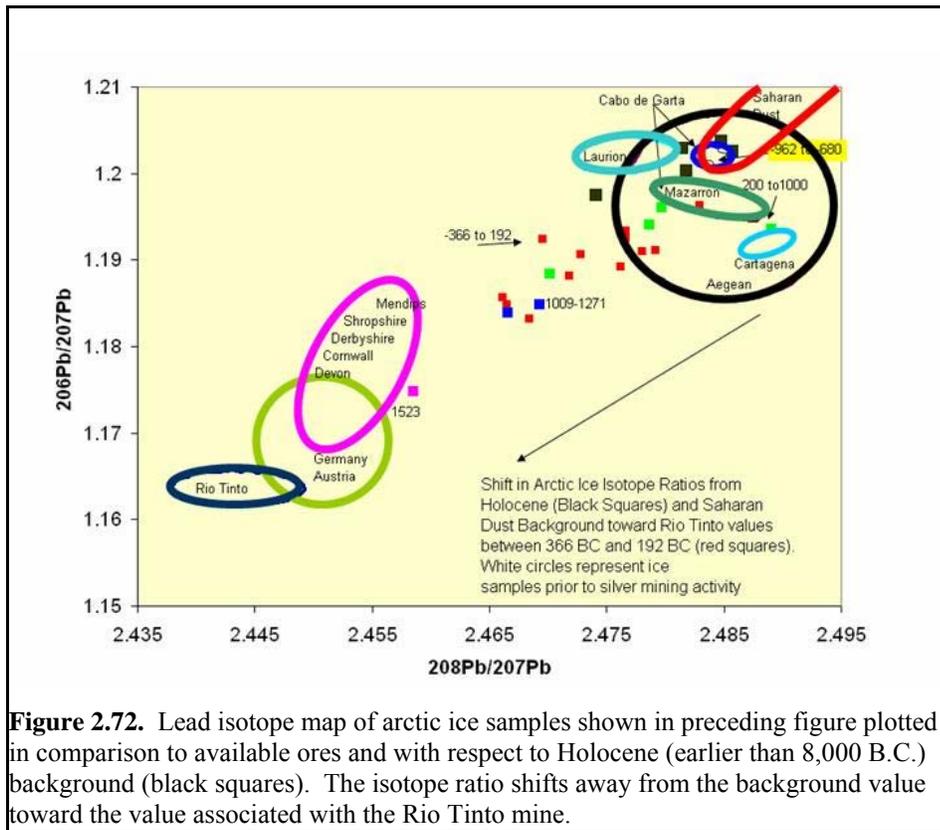
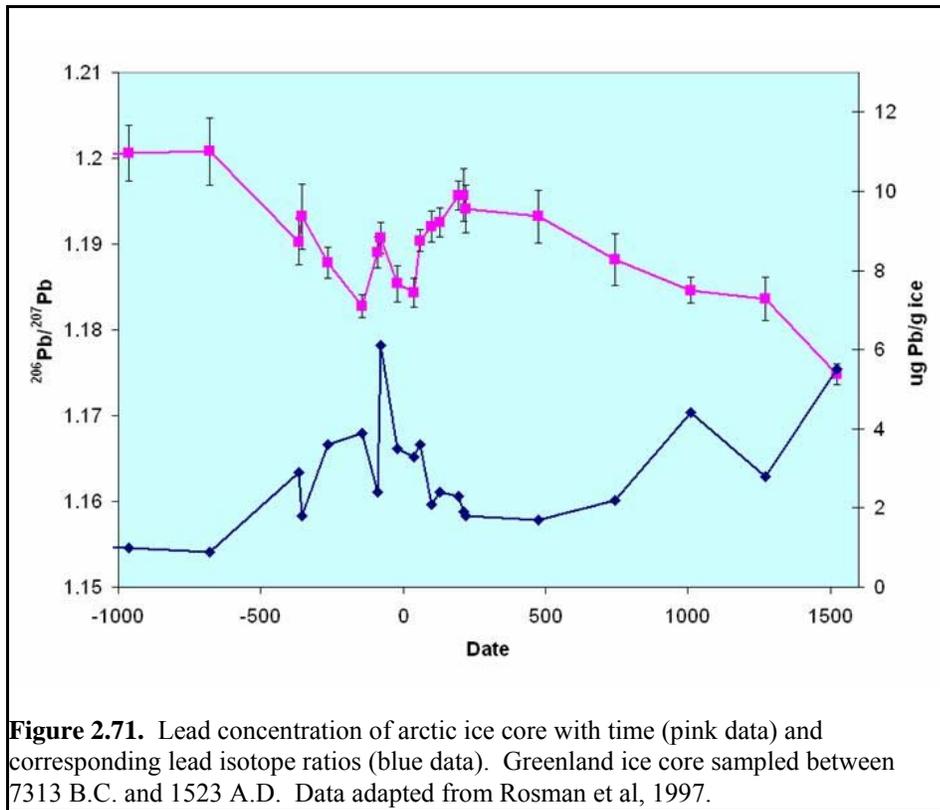
**Figure 2.70.** Phase diagram for gold in mercury. Stability of crystal forms and liquids as a function of concentration (x axis) and temperature (y axis). Source: Phase Diagrams for Binary Alloys. H. Okamoto, ASM, Materials Park, Ohio, 1995.

oral records of mining. The slag or discard heaps of the mines leave a record. More recently, as analytical methods have improved metal deposits in the Arctic ice can be used to recreate a metal balance of total lead produced, as well as that metal's isotopic signature. The total lead burden tracks very well the major phases of silver mining activity in Europe (Figure 1.3)(Hong et al., 1994). The record shows the beginning of the Laurion Mine activities, the huge output of the Romans, the small blip of the German mining and the advent of the industrial age. The amount of lead produced from the New World silver mines does not parallel that of Greek and Romans. This result is due to the mercury refining techniques used in the New World.

In addition to showing a total mass output record, the Arctic ice can track the location of lead sources by means of isotope ratios (Figure 2.71)

(Rosman et al., 1997). Not surprisingly, the major output of lead from the Romans includes sources from all of the known lead mines. However, a large amount of it derives from Spain, most of it from Rio Tinto silver mines, with some admixture from Cartagena (Figure 2.72).

Isotopic evidence from smelted ore is not admissible unless it keeps the same isotopic composition during the manufacturing process. This requirement has been shown to be true, both experimentally, and theoretically, as described in Example 2.4.

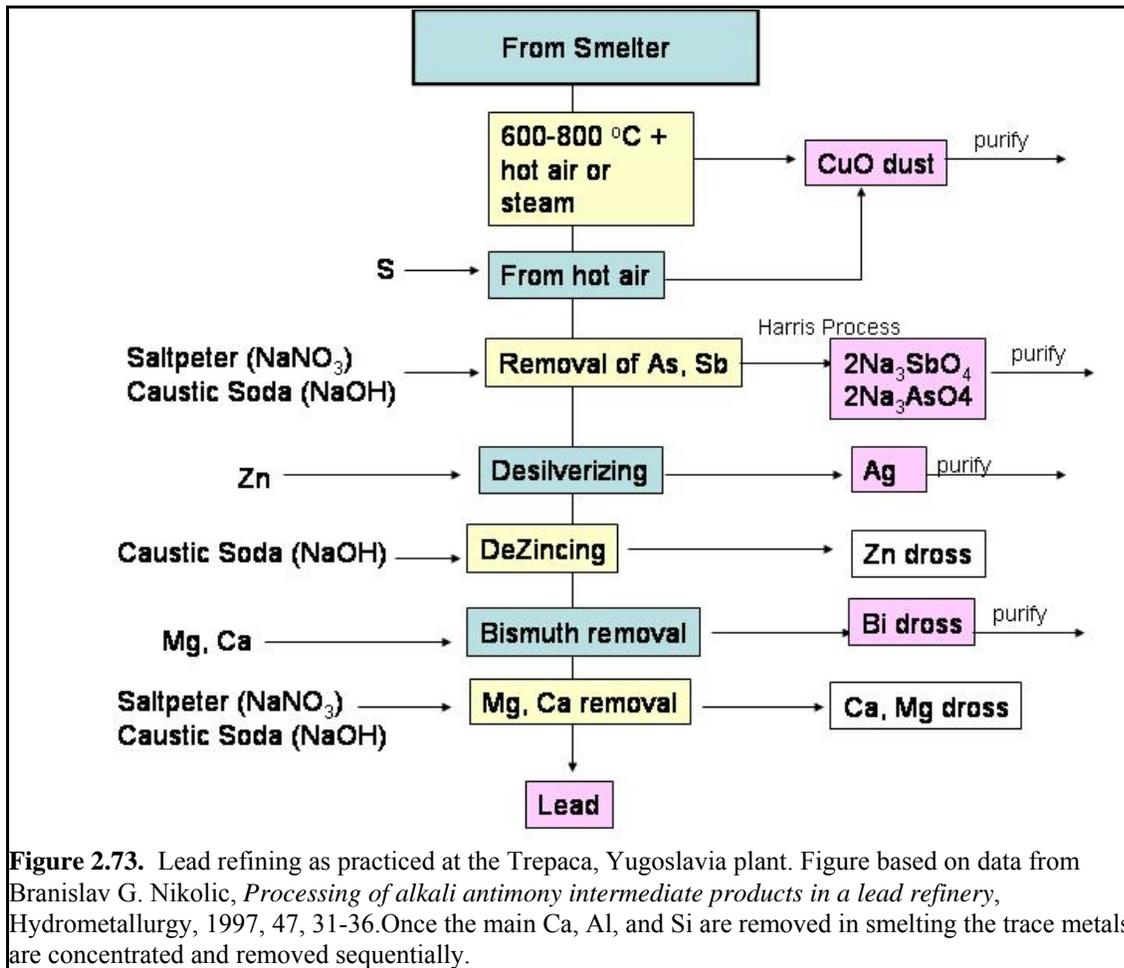


## Modern Metallurgy of Lead

Modern refining techniques for lead are numerous. In the Pattinson process, lead is slowly recrystallized on cooling. The pure crystals of lead can be swept off the top of the cooling metal, p. 11. The similar Parkes process is used to remove copper from the melt. The Betts process involves use of two lead electrodes. The anode, which removes electrons from the solution and converts the metal to a cation consists of the metal to be refined. The cathode is made of pure lead. Through it soluble lead ions obtain electrons to form solid lead metal. The solution between the two electrodes is composed of a lead fluosilicate and/or a lead fluoborate.

The Parkens zinc-desilvering process is a high-temperature process in which lead is melted, then cooled to a temperature lower than the freezing point of

copper. The crystallized copper floats on top of the lead and is skimmed off along with nickel, cobalt, and zinc. The lead metal mixture is reheated and oxidized to form crystallized oxides of antimony and arsenic (Figure 2.73). These oxides are also skimmed off. Finally, small amounts of zinc are added to the molten lead. Gold and silver particles partition from the liquid lead to the liquid zinc. The temperature is allowed to drop to 370°C (above the freezing point of lead). The zinc, gold, and silver precipitate and float above the dense molten lead then in the final step, remaining zinc is removed by evaporation at 500°C under a vacuum.



**Figure 2.73.** Lead refining as practiced at the Trepaca, Yugoslavia plant. Figure based on data from Branislav G. Nikolic, *Processing of alkali antimony intermediate products in a lead refinery*, Hydrometallurgy, 1997, 47, 31-36. Once the main Ca, Al, and Si are removed in smelting the trace metals are concentrated and removed sequentially.

## Chapter 2: Problems

- What is the typical temperature of a normal wood burning fire?
  - 600C
  - 1000C
  - 100C
  - 273C
- What advantage does the two tier kiln have over a hilltop furnace?
- What periodic trends are followed in melting points?
- Which will have a lower melting point, an  $s^2d^3$  or  $s^2d^6$  metal?
- Why is the appearance of metallurgy linked to the development of pottery?
- Mesopotamians were more/less likely to use lead because of their proximity/distance to lead ores.
- Porcelain has a fired porosity of about 1, 20, 0.05, 0.2%?
- List Patterson's four steps for the development of metallurgy.
- Explain why copper was manipulated into objects before gold?
- What is the reason for the 3000 year "lag" between "Old" and "New" world metallurgy?
- On a map of the world indicate regions likely to have been arable (farmed) with stone, bone tools in 10,000 B.C.
- What kinds of bones make the best cupels?
- What is the compound derived from the ashing bones? Why is it added to the melt in cupellation?
- Which source would be most trustworthy for technical information? Mappae Clavicula or Theophilus? Why?
- Why can gold not be separated from silver during cupellation?

- What role does lead play in cupellation?
- If an unknown metal oxide, MO, had a melting point of  $750^{\circ}\text{C}$  and a density of  $9\text{ g/cm}^3$ , could it be separated from gold?
- What were the three major lead mines in the Roman world?
- How much silver could be obtained from most galena ore bodies?  
Fill in the Table:

| Source                                      | oz Ag/ton |
|---|-----------|
| Laurion, Greece                             |           |
| Rio Tinto                                   |           |
| Leadville, Co., 1880-1900                   |           |
| Medina's estimate for successful cupellaton |           |

- Which mine was preferable to the Romans: Laurion, Greece, or Rio Tinto in Spain? Why?

### Problems Suitable for Those with more chemistry background

- Determine the relative velocities of  $\text{Cu}^{63}$  (69.09% abundant, mass 62.9298) to  $\text{Cu}^{65}$  (30.91% abundant, mass 64.9278) that would be produced during an effusive experiment. Would it be possible to change the natural isotope ratio of Cu during smelting?
- At what temperature does  $\text{Ag}_2\text{S}$  roasting to AgO become energetically favorable? Follow the example for PbS.

**Table 2.14**

| <u>Ore</u> | <u>formula</u>                         | <u>density (g/cm<sup>3</sup>)</u> | <u>melting pt<sup>o</sup></u> |
|------------|--|-----------------------------------|-------------------------------|
| <u>C</u>   | <u>boiling pt<sup>o</sup> C</u>        |                                   |                               |
| malachite  | $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$  | 4.0                               | Decomposes 200                |
| azurite    | $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ | 3.88                              | Decomposes 220                |
| Cuprite    | $\text{Cu}_2\text{O}$                  | 6.0                               | 1235 1800                     |
| chalcocite | $\text{Cu}_2\text{S}$                  | 5.6                               | 1100 ...                      |
| Cu         | Cu                                     | 8.92                              | 96 1083 2567                  |

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