

CHAPTER 4

The Wedding (Glasses and Glazes)

*Therefore, thou gaudy gold, Hard food for Midas, I will none of thee
Nor none of thee thou pale and common drudge
Tween man and man: but thou, thou meagre lead
Which rather threaten'st than dost promise aught,
Thy palidness moves me more than eloquence and here chose I.
Joy be the consequence*

Shakespeare Merchant of Venice

This chapter examines two interrelated uses of lead: glass technology and glazes. Why was lead and not some other material used in these technologies? How did the technologies spread?

It will be shown that lead was used for similar reasons as in metallurgy (energy conservation, among others) and that transmission of technology follows an East/West and West/East configuration, consistent with trends discussed in the preceding chapter. Time lines of events in the “Mesopotamian”, “Egyptian,” and “Classical” worlds are given in Appendix J, Tables 4.1-6-9. It may be useful to compare these time lines to the Chinese time line, Table J.5.

Why Lead?

According to recent studies, litharge (lead oxide), the byproduct of silver mining, was recycled in the glass industry. The evidence comes from the similarity of metal content in the litharge obtained from purifying silver and the metal content in glass and enamels.

A particular link between metallurgical slags and glasswork has been suggested for the Anglo-Saxon glass enamels. Enamelled metalwork from Celtic Britain used opaque red glass. Opaque red glass used in this enameling consisted predominately of copper ($\text{Cu} + \text{CuO} + \text{Cu}_2\text{O}$) that reportedly was 5-10% CuO and 20-30% PbO in a soda (Na_2O)-lime (CaO)-silica glass base. After the Roman occupation of Celtic lands, the color ranges were extended but an alternative chemical composition (<10% PbO) was used. Post-Roman enamel glass is low in Na_2O (<0.2%) and lime. The glass is also more heterogeneous than other ancient glasses. Relatively

high concentrations of Sn and Zn are also present..

The low Na_2O content implies that Anglo-Saxon glass technology did not derive directly from that of the Roman period, which utilized soda glass. The high Sn/Zn content suggests the use of recycled metallurgical material. This hypothesis is supported by the similar composition of early medieval red enamel glass to that of 3rd century A.D. German slags. In the German metallurgy of the time, a regular cupellation was blended with scrap metal to produce litharge up to 2% ZnO and 10% SnO_2 . A 10th century Anglo-Saxon site shows evidence of a similar metallurgical process with trace scrap litharge very high in Zn, Sn, and As as well as dissolved grains of quartz. Perhaps early German use of litharge in glasswork continued into the

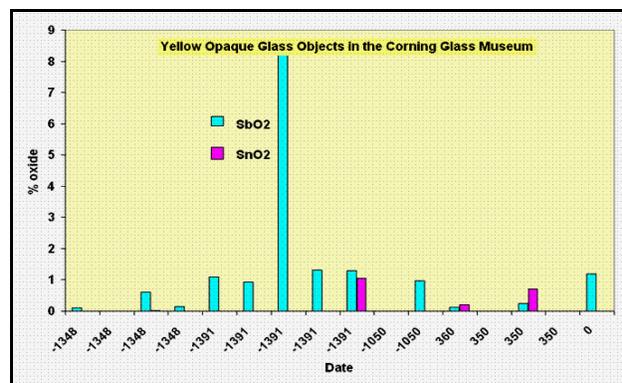


Figure 4.1. Glass in the Corning Glass museum shows an change in chemical composition of yellow glasses that corresponds to the fall of silver mining activity in the Roman Empire.

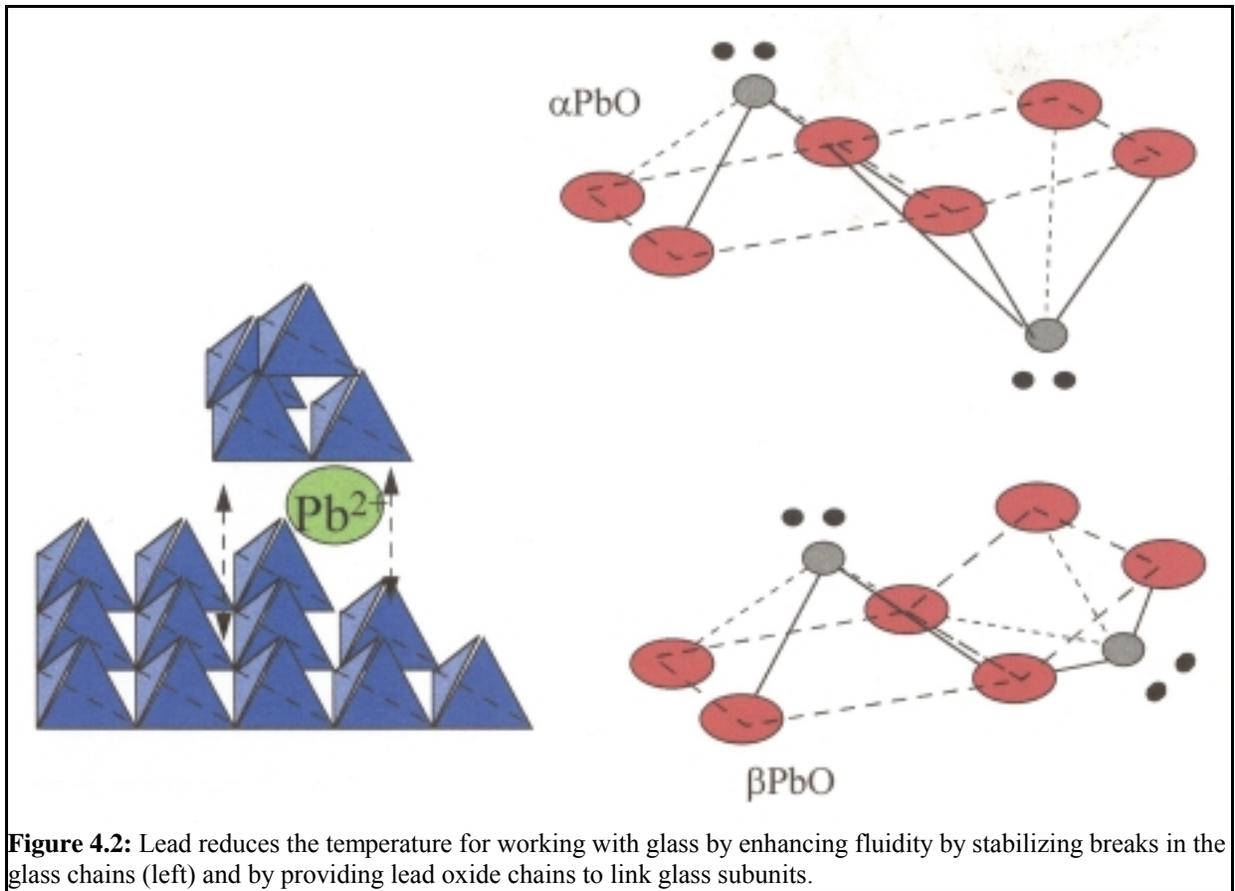


Figure 4.2: Lead reduces the temperature for working with glass by enhancing fluidity by stabilizing breaks in the glass chains (left) and by providing lead oxide chains to link glass subunits.

late Anglo-Saxon period (Stapleton et al., 1999).

Another piece of evidence for recycling of lead oxide from silver mining for the glass industry is the variation in antimony (Sb) in glasses. Many of the silver ores are associated with antimony. Common silver ores are argentite (Ag_2S), miagryrite (AgSbS_2), matildite ($\alpha\text{-AgBiS}_2$) and aramaysite ($\text{Ag}(\text{Bi},\text{Sb})\text{S}_2$). The peculiar use of Sb as an opacifier and of Pb+Sb as a yellow colorant would be the natural outcome of metallurgical practices associated with silver mining. The loss of Pb/Sb glasses around 400 A.D. would also correspond nicely with the fall in production of the Rio Tinto silver mines (Figures 1.3 and 4.1).

Why would ancient technologists recycle the lead byproduct of silver mining into the glass industry? The primary reasons are a reduction in energy use and the increased ability to control the fluidity of the glass melt. These two reasons derive from the structure of lead oxide as a chain forming material and to the ability of lead to stabilize breaks in the three dimensional structure of glass (Figure 4.2).

GLASSES

Desirable Properties of Leaded Glass

Lead and glass-making are even more historically intertwined than lead and metallurgy. This is because lead imparts several desirable properties to glasses.

1. Lead renders glass less viscous and thus easier to work with at lower temperatures. Energy costs are reduced.
2. Lead lowers the heat of expansion of the glass and reduces cracking upon cooling.
3. Lead oxide modifies the electrons on oxygen to promote a high refractive index. The product is a brilliant, jewel-like glass.
4. Lead is a good medium (solvent) for Cu_2O , a red compound used in making colored glasses. The presence of lead oxide modifies the basicity of the silicate backbone of the glass and allows copper to move through the glass to nucleating sites where dendrites of Cu_2O form, giving rise to the color red.

5. Lead forms a very brilliant yellow compound when combined with antimony, to make yellow glasses.

Ancient Leaded Glasses

The history of glass is nearly as old as the history of metals (Grose, 1989). Glass-making appears in the Western world during the late Bronze Age (1600-1200 B.C.) in the northern Mesopotamian Hurrian kingdom of Mitanni. Glass was highly desirable as a substitute for extremely rare blue lapis. Object manufacturing, namely that of vases, began around the middle of the 16th century B.C.E. A core was made out of mud and clay around a metal in the shape of the desired object, then dipped in hot glass. The walls were made even by rolling the vessel back and forth on a flat stone (Figure 4.3). Decorative threads could be added as the object was rotated. After annealing and cooling the core was scraped from the interior.

An Egyptian glass industry also flourished during this time period. A dramatic upsurge in technology was associated with the New Kingdom of the 18th dynasty (1570-1305 B.C.E.). This was connected to the successful military campaign of Thutmose III (1490-1436 B.C.) Palestine and Syria. The campaign brought captured Asiatic glass-makers into Egypt and established peace necessary for major trading. Figure 4.4 is an Egyptian glass core wrapped vase [Brill, 1974 #1995, p. 9-25]. The yellow colors are from lead antimonate and the red colors from Cu_2O in leaded glass. A clay table from Tell Unar (1400-1200 B.C., Middle Babylonia) gives a recipe for red glass:

For each mina of zukâ glass (you take) ten shekels of lead, fifteen shekels of copper half (zûzu) a shekel of anzahhu-glass (and) [half a shekel] of antimony. This is the method for Assyrian red stone glass.

This first wave of classical western glass-working was lost in 1200-1100 B.C.E., when the leading centers of the Bronze age collapsed under famine and war. The Mycenaean and Minoan communities of Greece, Crete, and Cyprus vanished altogether. Egypt was attacked in 1220, 1189, and 1186 B.C. by unrelated groups massing in Libya.

The Iron Age (900-400 B.C.) brought on a cultural revival. The new states of Nineveh,

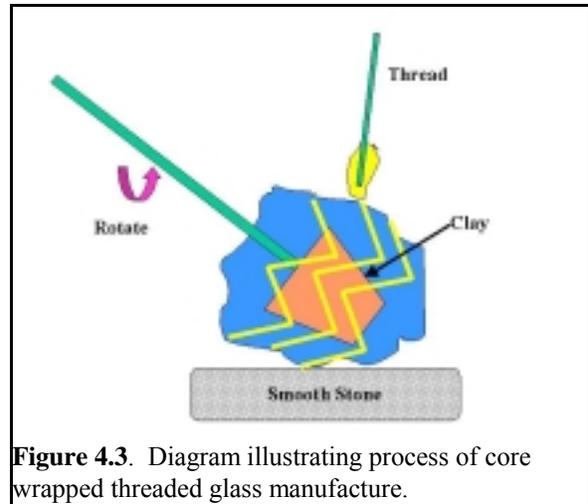


Figure 4.3. Diagram illustrating process of core wrapped threaded glass manufacture.



Figure 4.4: Egyptian Vase core-wrapped vase: 1300 B.C., Corning Museum of Glass, with permission.

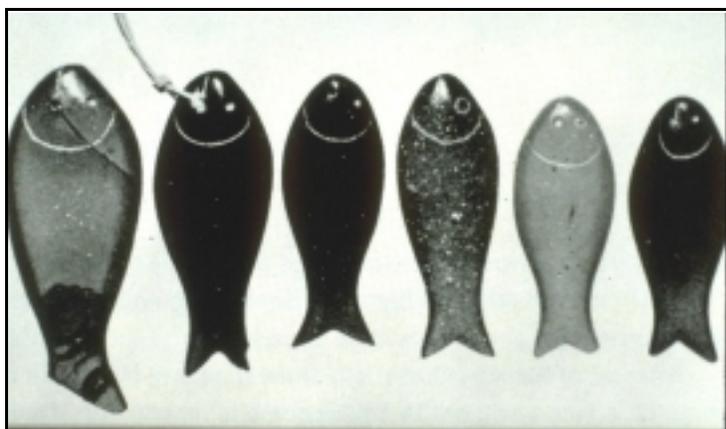


Figure 4.5. Japanese fish pendants (752 A.D.) left to right: blue, yellow, green, dark green, dark green, and green. All but blue are 70% PbO. From: Kazuo Yamasaki's *Technical Studies on the Ancient Art of Japan*, in *Application of Science in Examination of Works of Art*, 1965, p. 123.



Figure 4.6. Roman-Celtic brooch with yellow and red glasses (Author).

Babylon, Tyre, Sidon, Greece, Phoenicia, and Etruria took the place of older ones. The new cultures left records of their technologies in libraries. The palace library of the Assyrian king Assurbanipal 668-627 B.C. held several glass recipes in clay cuneiform.

(These recipes were later translated into Greek and Latin, then passed onto the libraries at Alexandria, and carried to the Dark Age monasteries in Europe. There they were copied and preserved by monks who were

illiterate about the technology.)

The glasses of the Iron Age were still the norm. They were used to hold expensive oils, perfumes, and unguents. Some of these glasses may have been traded to China, as the composition of Loyang (400 B.C.). Glass beads is spectroscopically identical to that of Egyptian beads (Caley, 1962; Watson, 1984).

Figure 4.5 shows several examples of glass from the Shōsōin an 8th-century temple of the Great Buddha in Nara, Japan. Japan may have derived its glass making technology from China. These fish pendants are colored as follows from left to right: blue, yellow, green, dark green, dark green, and green. All but the blue one are 70% PbO. The Shōsōin Repository was a storehouse of the temple. It included one set of objects offered to the Great Buddha by the Empress Dowager Kōmyō (701-760 A.D.) in 756 A.D. after the death of the Emperor Shōmu. Another set comprised objects used at the "eye-opening" ceremony of the Great Buddha in 752 A.D (Yamasaki, 1965).

Hellenistic glass-making spread throughout the Mediterranean/Middle Eastern area as Alexander the Great's empire was carved up among generals (323 B.C.) and glass-makers went to Ptolemaic Egypt. The early Roman Empire acquired these glass-working skills with incorporation of Hellenistic states (2nd and 1st centuries B.C.). Roman glass-working may have originated in the technical knowledge of war captives. An alternative explanation is that the spread of glass-working was related to Jewish migrations. Jews had been populous in Alexandria where they learned the art of glass-making. They were mobile and linked to other Jewish populations in Sidon and Syria (Neuburg, 1962, p. 53).

Glassblowing was discovered about the 1st century B.C. in the Syro-Palestinian area of Phoenicia. Famous glass-makers of the era were Artas, Philippos and Neikon from the city of Sidon in Phoenicia. The signatures of the glass-makers Aristreas and Ennion are found on mold-blown glass vessels in northern Italy, suggesting that they moved from Levant (Tait, 1991, p. 70). After the Roman conquest of Alexandria in 30 B.C., glass began to arrive there, including the first examples of blown glass in 20 A.D. Alexandrians founded glassworks between Cumae and Liternum and in Rome. Pliny mentions the influx of glassblowing Syrians into Rome. By the time of Alexander Severus



Figure 4.7. The Castle-Newe armlets ascribed to 50-150 A.D. The yellow is lead antimonate. John Brailsford's *Early Celtic Masterpieces from Britain in the British Museum*, p. 71.



Figure 4.8. Opus Sectile of Thomas from the 2nd half of the 4th century A.D. In Donald B. Harden's *Glass of the Caesars*, 1987, Plate 11, p. 34.

(222-235 A.D.) Roman glass-makers were subject to a high tax until Constantine repealed it.

Roman glass was exported throughout Europe

(see Roman trade map, Figure 2.18). Figure 4.6 a Romano-Celtic brooch inset with yellow glass. Figure 4.8 shows the Castle Newe Armlets, cast by the lost wax method, dated back to 50-150 A.D. The

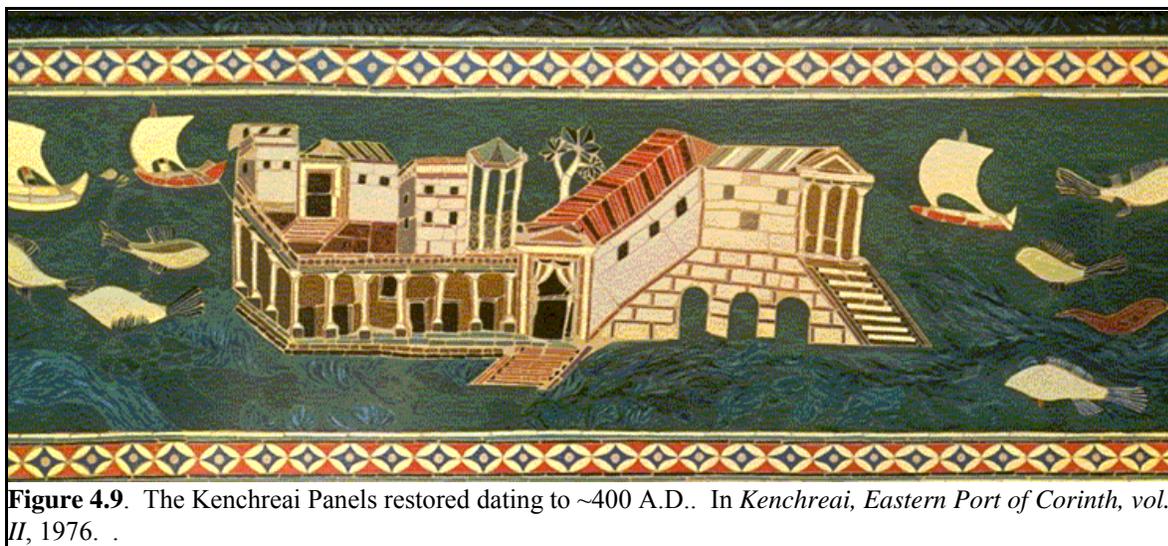


Figure 4.9. The Kenchreai Panels restored dating to ~400 A.D.. In *Kenchreai, Eastern Port of Corinth, vol. II*, 1976. .

checkered red and yellow glass is set in the center. The yellow glass is composed of lead antimonate (Brailsford, 1975). The Battersea Shield, the best-known piece of early Celtic craftsmanship from Britain was recovered from the River Thames at Battersea in 1857. The shield's art motif suggests Roman influence. The Battersea Shield likely came very late in the period of early Celtic art (100 A.D.?). The red ornamental inlays have been chemically analyzed. The composition of all 33 specimens followed a uniform pattern with average values of about 7% cuprous oxide (Cu_2O) and 25% lead oxide (PbO). This constancy in composition is thought to be deliberate. A block of raw glass from Tara Hill has the same chemical composition as Iron Age bronze samples. Significantly the isotope ratios in the Tara Hill glass suggest that its lead content came from Italy.

The raw glass would then have reached Britain and Northern Europe through trade, where it could be broken down into smaller lumps and used by a glassworker to decorate the bronzes of this period (Hughes, 1972).

Red glass was also used in glass mosaics in the Roman Empire's Greek provinces. An intact mosaic dating from 450 A.D. was recently excavated at the port of Kenchreai (450 A.D.) (see map Figure 2.18, Roman trading) (Chicago et al., 1976). The mosaic is shown in its restored form in Figure 4.9. The red glass of this mosaic is leaded red glass (Scranton and Ramage, 1967, p. 124). It contains > 1% lead oxide. Its copper content (Cu , CuO , Cu_2O) is reported to be

2-3% CuO . Lead is used to facilitate the growth of copper oxide in the glass.

Fragments of yellow glass from the mosaic have been found to contain 6-14% PbO with < 1% Sb_2O_5 and 1-3% SnO_2 . The presence of both tin and antimony in the mosaic indicates that the mosaic marks the transition between lead antimony and lead tin as a yellow pigment.

A similar mosaic dating from the late 400s A.D. is that of the *opus sectile* Panel with Thomas (Figure 4.8). The chemical analysis of this panel matches that of the Kenchreai glasses. The lead isotope ratios of the glasses and the mineralogical characteristics of the earthenware both support the suggestion that the panels were made in the same region (Harden, 1987).

Some particularly beautiful examples of lead containing Roman glass work are the Portland Vase (Figure 4.10) and the Auldo Jug (Figure 4.11) (Harden, 1987). Both of these objects were cast in two layers: a blue background with opaque white (lead oxide) glass on the top. The white glass is cut away, cameo style, to give a relief of the object, a bust. The Portland Vase's white layer consists of 12% lead oxide, while that part of the Auldo Jug from Pompeii consists of 23% white lead (Rooksby, 1959). The lead in the glass made it very much easier to carve the intricate designs of the cameo-decoration.

Syrian and Jewish glass-workers arrived in the Roman Empire from the Mideast and were initially concentrated in the central part of Italy. In the first century A.D., Italy exported glass into Gaul. Shortly afterwards, glass-workers moved north into southern

France and the lower Rhone Valley, founding glasshouses in Boulogne, Amiens, Namur, and Rheims. At the same time potters began moving out of central Italy, which suggests that the move was driven not by a shortage of raw materials (which differed between the two) but by a lack of fuel (Perlin, 1989, p. 123)). The Gallic provinces also lost their woods. Competition for fuel in southern France forced the glass-makers and potters to move once again, this time to Belgium and Germany. By the end of 300 A.D., no trace of French glass-making remained.

Glass-making retained Middle Eastern characteristics such as mold-blowing and grape-cluster shapes (Neuburg, 1962, p. 87). Glasswork continued, as shown by grave deposits, but the quality began to decline in the 400s. The art of red glass-making was lost. At the end of the Frankish-Merovingian period (400-741 A.D.), the Western Church prohibited the use of glass in liturgy because of its fragility. The church also condemned the practice of grave deposits. Only the stained glass of the cathedrals remained as an outlet for glass. Gregory of Tours in 500 A.D. had glass installed for St. Martin Cathedral of Tours. In England, Abbot Benedict Bishop of Monkwearmouth commissioned French glaziers in 670 A.D. for monastery stained glass windows (Frueh and Frueh, 1998).

The surviving part of the Roman Empire, its eastern half, was more cosmopolitan. It retained a market for non-church luxury items, including the intricate glasswork of the Romans. Perfume bottles with basket handles and trailings were a staple of the eastern glass-makers. Constantine exempted glass-workers from certain taxes. Years later, Theodosius, in his *Codex*, eliminated glass-workers entirely from taxation. Glass-workers were encouraged to make their homes in Constantinople in 551-565 A.D. under the reign of Bishop Menas.

The glass-working tradition of Constantinople was incorporated into that of Venice by 900 A.D. The story of Venetian glass-making began in 500 A.D. when Theodoric, the barbarian king, appreciated the value of the timber-producing region in the Po River watershed (Figure 4.12). Theodoric used the region's abundant timber to build a fleet of several thousand ships. This fleet allowed trade in the Po valley to have a maritime basis. Much later in the twelfth century, shipbuilding was consolidated under a state-run center,



Figure 4.10. The Portland Vase. The white surface is 12% lead oxide, cut away on blue surface as a cameo. It dates to the first century B.C., Rome. From Donald B. Harden's, *Glass of the Ceasars*, Olivetti, 1987. British Museum 1945. 9-271

the Arsenal (Arabic for "House of Construction") (Perlin, 1989, p.146).

Early trade involved the export of Slavic and northern slaves to Muslim Africa, including eunuchs for Eastern courts. Trade also involved lumber from the Po Valley, one of the remaining sources of timber (oak, ash, beech, larch, pine, and fir). The return goods included gold, silver, spices, and luxury goods from the East.

Armored knights first appeared in the French/German region of the Carolingian court about 732 A.D. and they played an important role in the development of Venice. The combat style these knights was to charge the foe on horseback carrying a spear lodged under one arm. They braced themselves for impact by leaning forward over their horses. This type of fighting was difficult to defend against. It allowed the Norman/Franks to take and sack Rome in 1059, again in 1094, and to move into northern Italy at

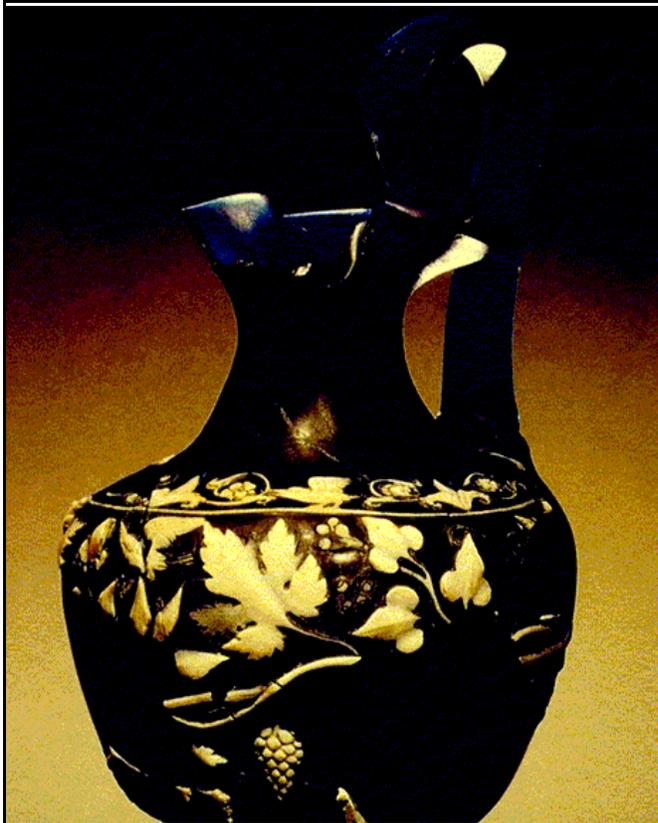


Figure 4.11 The Aldo Jug from the late 2nd quarter of the first century A.D., Pompeii. The cameo surface is 23% lead oxide. From Donald B. Harden's *Glass of the Caesars*, 1987. British Museum GR 1840 12-15.41

the same time that the Normans were moving into Sicily. The Franks intended to move against the Byzantine Empire with this style of fighting. This plan required them to launch a fleet from the Po Valley. The death of Robert Guiscard temporarily gave the Venetians and Constantinople a respite in which they could form an alliance. The Venetians agreed to support Constantinople in return for a free trade agreement (McNeill, 1974, p. 3). In 1082, Emperor Alexius granted Venetians full exemption from all excise taxes in Aegean and Mediterranean trade. The tax exemption allowed Venetian merchants to become the undisputed economic masters of the region.

The sea power of the Venetians allowed them to play a strategic role in the crusades and to exact control of important cities in exchange for their military help. Venetians acquired the cities of Acre and Tyre, where they made further contact with glass-makers (Lane, 1973, p. 72).

Glass-makers from the East began arriving in

the area by 900-1100 A.D. In some cases, they brought sand from Belus and from the desert between Alexandria and Cairo (Neuburg, 1962, p. 91). The movement of glass-makers was accelerated by the sack of Constantinople in 1204. In 1268, the Venetian glass-makers were well enough established to participate in the Doge's inaugural parade, carrying water bottles, scent-flasks, and other such graceful glass objects (Tait, 1991, p. 149). In 1271, the glass-makers' Capitulare was approved, creating a privileged position, and prohibiting importation of glass or immigration of foreign glass-makers. By 1279 the glass-workers in Venice had formed a guild. By 1282, glasses were being exported in large quantities through German merchants. Ships from Venice were selling Venetian glass in the Port of London by 1399.

A single group worked all phases of the glass manufacture. Three different types of furnaces were required. One was for purification, i.e. gas removal, at low temperature, a process known as fritting. The second was the main furnace, which had temperatures high enough to fuse silicon, limestone, and soda (Figure 4.13). In this furnace, glass was blown. The side of the furnace required a number of openings for teams of glassblowers to work. A team consisted of a chief glassblower and 3-5 assistants. The third furnace was used to gradually cool the glass for tempering, a gradual cooling of the glass. It was attached to the main furnace to make use of the heat.

In 1291, the glass-workers were compelled to move out of the city proper onto the island of Murano because their work posed a fire hazard. Murano became known as the center for production of imitation pearls and gems, enamels, lenses for astronomical tools and eyeglasses (1302 A.D.), and window panes. The most famous of the Venetian glass beads were the Chevron beads. They were traded as far afield as Africa and China. These beads are canes of colored blue, red, and green glass divided by thin layers of opaque white glass. The result is a star-shaped pattern.

Glass-workers on Murano were subject to city control over their travels. If they left the island, they forfeited their rights as guild members. By 1365, glass-makers could not work outside Venice or take their skills elsewhere (Mackenney, 1987, p. 18). The goal was to retain control over the production secrets of these highly valuable artists (Moore, 1935, p. 29). In return for these restrictions, the city-state applied large import duties on foreign glass and gave glass-makers un-precedented mobility into the upper classes. Glass

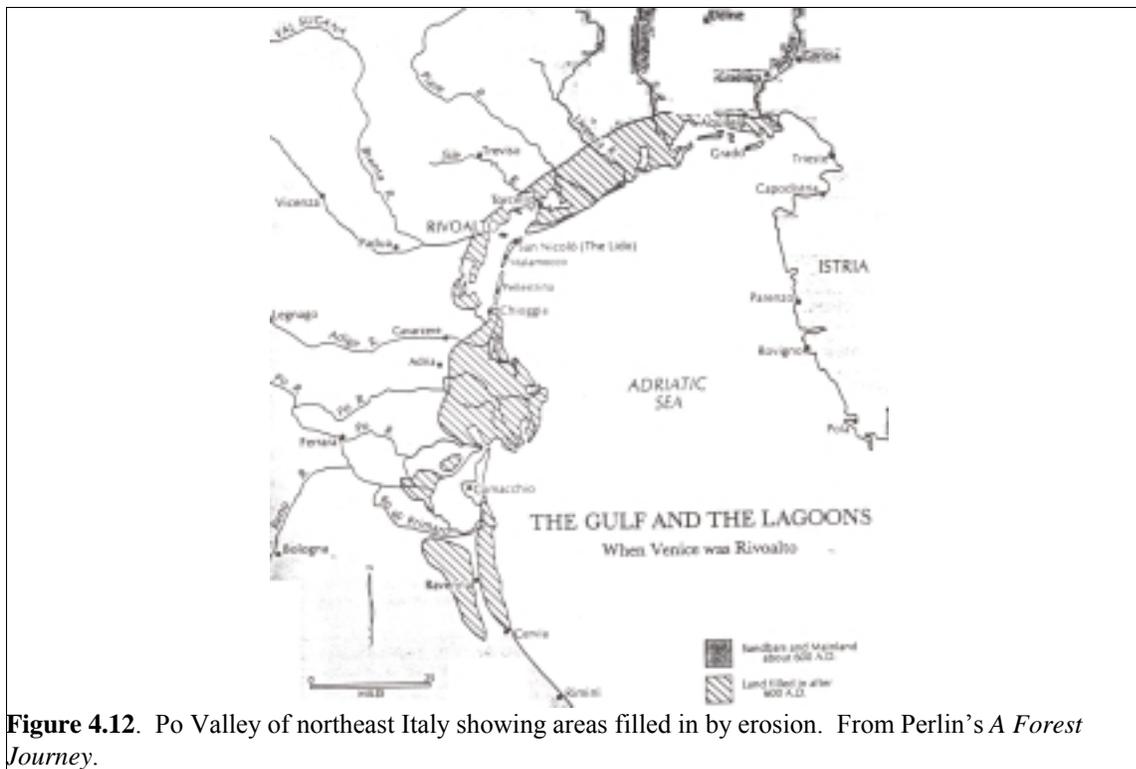


Figure 4.12. Po Valley of northeast Italy showing areas filled in by erosion. From Perlin's *A Forest Journey*.

making was deemed a valuable profession because it used skills inherited from the eastern empire as well as expensive raw materials.

Material for the glassworks included sand washed from the Alps (especially the Adige River in Verona), and soda ash from high-sodium plants, as opposed to potash from high-potassium trees. Potash was the source of material for the northern (German) glass makers. Soda ash was obtained from Syrian seaweed ash (Lane, 1973, p. 160). The use of Na^+ instead of K^+ had an important impact on the glassworks' fluidity and strength. As a result, the Venetians were able to position themselves as the leading makers of clear and brilliant glasses. Soda lime was obtained from marine plants in salty marshes. The *barilla* in Alicante, Spain, was regarded as the best source. The state mandated the quality of any raw materials purchased because the final product had to bolster the reputation of Venetian glass. In 1306 and again in 1330, alum from Alexandria was forbidden because of its poor quality (Tait, 1991, p. 149).

Wood from Friuli and Istria was used, although by 1200s the abundant wood of the Po Valley had been decimated by shipbuilding and commercial activities. Figures 4.14 and 4.15 show the deforestation of the hills above Venice. The

deforestation was so extensive that the coastal areas began to fill in (Figure 4.12). This had happened as well during the Roman deforestation of Spain near the Rio Tinto silver mines. The 20 furnaces at Murano burned day and night. A fuel provisions supervisor might have removed 12,000 carloads of wood in a single trip to the forest (Perlin, 1989, p. 154). Potters and glass workers were required to cease activities in December and January. These restrictions on working months may have been related to fuel economics (Mackenny, 1987, p. 17).

Venetian glasswork evolved into highly painted (enameled) ware that paralleled motifs from the Islamic world. A series of enamellers came to Venice between 1280-1348 A.D. from the Byzantine Empire, including the Corinthian Greek Gregorio da Napoli, and the Dalmatians Barolomeo and Donino da Zara. These glass makers became known as the Aldrevandino Group. Their glass-enameled beakers competed well with silver and gold ones. These beakers have been found in Ireland, Sweden, Palermo, Egypt, and the Caucasus.

In 1380 A.D., Venice achieved maritime domination over Padua. A famous glass maker from that time was Angelo Barovier (d. 1460 A.D.). His work was so good that the Duke of Urbino gave him



Figure 4.13. Glassmaking in Venice as illustrated by Agricola.

permission to use his glass furnaces for producing *crystallo* (1457 A.D.).

By the early 1500s, Venetian glass working was at its peak of fame. In addition to the rock crystal used to imitate eyeglasses, the Venetians could make highly accurate navigational hourglasses (Lane, 1973, p.310). It could be argued that the glass makers of Venice furthered exploration through their development of lenses and hourglasses. They excited the admiration of Agricola so much so that he devoted two years to study in Venice:

Glassmen make a variety of objects: cups, phials, pitchers, globular bottles, dishes, saucers, mirrors,

animals, trees, ships. Of so many fine and wonderful objects I should take long to tell. I have seen such at Venice, and especially at the Feast of Ascension when they were on sale at Murano, where are the most famous of all glass factories...

Florence established court glasshouses under the Grand Duke Cosimo I (1537-74 A.D.), luring the Murano glassmaker Bortolo d'Alvise. Antonio Neri, a priest, also worked in Florence. In 1612 A.D. he published his book *Arts Vetraria* in that city. Neri concentrated on the making of leaded glass because of the unusual brilliance of leaded glass lent itself easily to the counterfeiting of gemstones. His book was translated into English in 1662 A.D. (Charleston, 1960).

England at the time of Henry VIII exported lead, tin, and wood, and imported salt, dyes, glass, iron, and arms. During the reign of Henry the VIII the potential for a blockade by Catholic Spain, France and Scotland caused the king to develop an internal arms industry. He hired ironmaster William Levett to join forces with the country's gunfounders Peter Bawde and Ralph Hogge. These three established themselves in southern England, where iron ore was abundant and where oak woods had been re-established after Roman colonization (Figure 4.16). After the reign of Henry VIII, Elizabeth I also wished to alter the trade balance by creating internal industries. By 1549, there were eight glassmakers from Murano working under contract in London.

Elizabethan policy spurred home production of glass by granting monopolies on the production and sale of various glass types (173). These monopolies were awarded to foreigners with trade skills who then set up factories in England. One of them was the Venetian Jacob

Verselyne:

To make drinking and other glasses like those made near Venice and to sell them" so that they would be sold "as good cheap or rather better cheap than those hitherto imported from other part overseas..." John Stow, reported in the 16th century *"The first making of Venice glass in England began...in London, about the beginning of the reign of Queen Elizabeth.*

Religious persecution also brought skilled laborers to England. The Spanish Duke of Alba was busy stamping out Protestantism in Flanders on behalf of Philip II of Spain. Many Protestants from that

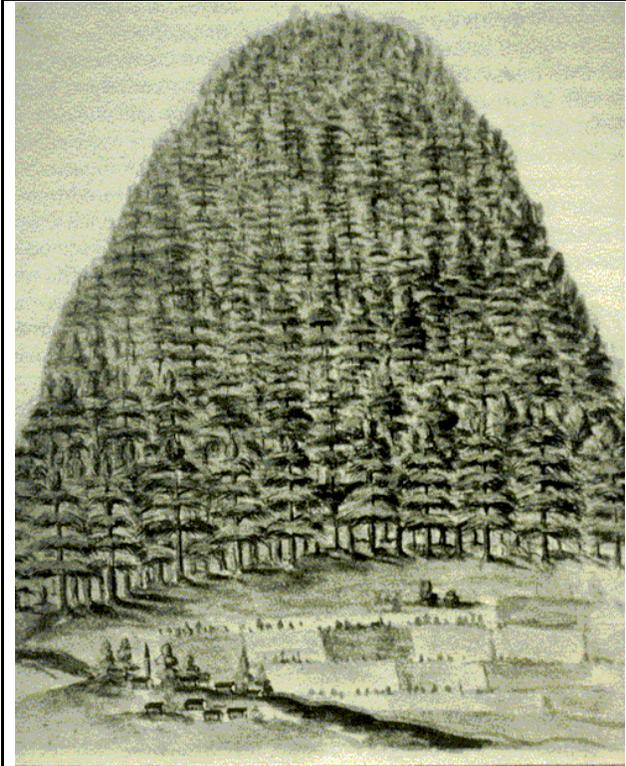


Figure 4.14. Venice in trees in 1600. The original draw by Giuseppe Paulini. In John Perlin's *A Forest Journey*, 1989, p. 156.

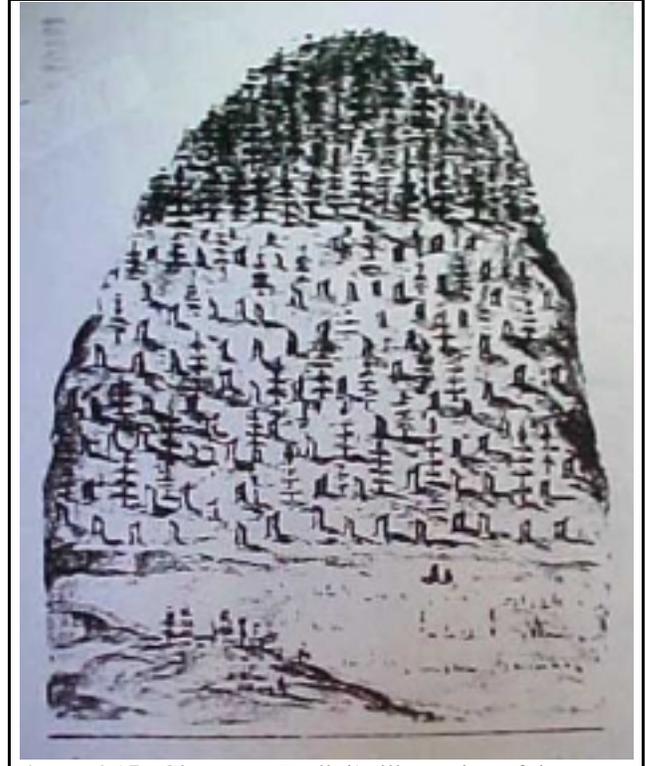


Figure 4.15. Giuseppe Paulini's illustration of the cutting of the woods near Venice, 1600. In Perlin's *A Forest Journey*, 1989, p. 157.

region sought asylum in England, including the glassmakers Jean Carre and Anthony Becchu, who obtained a monopoly for making window glass. By 1589, 14 or 15 glassworks were in operation. Only 30 years before, prior to Elizabeth's reign, no glass had been manufactured in England.

Glassworkers, like shipwrights, preferred mature hardwoods, meaning those at least twenty years old, to fuel their furnaces. The wood burned so quickly that the steward of one glasshouse in Kent wrote to his master: "If you will have the glassmen to continue at work, you must either grant more wood cutters be set to work...for all the cleft cords...are carried to the glass house already." A glasshouse, thus, needed a large supply of wood to stay in business. Some glasshouse proprietors moved their factories to follow the ever-diminishing woods (Figure 4.16).

The combined rise of arms, salt, and glass industries led to a large-scale loss of English forests. By the end of the 1570s, many forests and woods had been completely cut down and turned into charcoal. By 1608 A.D., wood for house fuel was not available to the ordinary population.

In 1615 A.D., James issued a proclamation called the "Bill for the Preservation of Woods". It forbade the use of wood as fuel in glass production.

The great waste of timber in making glass is a matter of serious concern" since "timber hath been of all times truly esteemed as the principal patrimony of this our realm of England and a precious inheritance of both Crown and Subject." For this reason, "it were the less evil, to reduce the times into the ancient manner of drinking in stone and lattice windows than to suffer the loss of such a treasure." The use of coal would stop the "waste of wood and timber hath been exceeding great and intolerable by the glass-houses and glass-works of late. No one is to make glass with timber or wood or any fuel made from them, and no one is to make glasshouses in which timber is used for fuel...upon pain of our indignation. (Perlin, 1989, p. 194).

The use of the coal furnace raised the temperature of the glass kilns pine wood which only



Figure 4.16. A map of the English forest region with the oak forests in the south. From John Perlin's *A Forest Journey*, 1989, p. 162.

gives -21.2 kJ/g of material, while bituminous coal gives -28.3 kJ/g of material. The coal furnace also changed the composition of the trace elements that could contaminate the glass melt.

Wood ash composition depends upon the specific nutrient cycling of the tree species (Tables C.10 and C.11). Nutrient cycling of trace minerals involves atmospheric input, rock weathering, plant uptake, leaf litter return to soil, plant harvesting, and leaching. Atmospheric input to the soil has been

calculated to be 1 to 10 kg/ha-yr of K, 3 to 19 of Ca and 4-11 of Mg (Ovington, 1968) in temperate climates. Average values across the world are 3.2 kg/ha-yr for K, 8.0 for Ca, and 2.8 for Mg. The amount of this material deposited in any given locale depends upon its proximity or lack of it to the ocean (Table C.3) (Pritchett, 1979, p. 193).

Greater amounts of these minerals are produced from weathering rock, as shown in Table C.2. From an undisturbed forest in New Hampshire, the amount of mineral lost to groundwater or stream flow is estimated to be an average of 2.0 kg/ha-yr for K, 11.4 for Ca, and 3.2 for Mg. Considerable amounts of these minerals are left to be removed by the plant or tree (C.10 and C.11). The exact quantities depend upon the soil, climate, and plant or tree species.

The removal of various nutrients by trees can cause a net loss of minerals from the forest soil. Typical values removed by different species are shown in Tables C.10 and C.11. These tables show that trees serve as a net sink for K, Ca, and Mg, as well as for trace minerals such as B and Zn. Depending upon its species and location, a tree will have variable ratios of K, Ca, and Mg, which will be retained in some proportion (dependent upon volatilization and ash loss) in the wood ash. The ash content will consist of K, Ca, Mg primarily with anions of primarily carbonates:

K_2CO_3 , $CaCO_3$ and $MgCO_3$. K_2CO_3 is known as potash.

In early colonial American, the potash industry involved clear-cutting and burning of logs, then collecting the ashes. The ashes were placed on a simple support of twigs/straw in a barrel with holes at the bottom. Water was poured in the top and collected at the bottom. The collected water was evaporated in an iron kettle to obtain a black solid consisting of the soluble salts and organic carbon. The carbon was



Figure 4.17. Ravenscroft leaded glass manufactured 1690. Figure from Hugh Tate's *Glass, 5,000 years*, 1991. British Museum 6925.2-16-1.

driven off by heating the metal pot. The remaining material, known as lye or potash, was used in soaps and gunpowder (Haynes, 1954, p. 27-29). As shown in Table C.11, the type of tree affected the final yield of potash.

The type of tree obviously can affect the ash content and thus the glassblowing process because the melt depends upon small metal impurities. The introduction of the coal furnace enabled better temperature control for annealing and reduced blown ash impurities.

The English coal-fired furnace produced a very robust dark green glass called "black bottle". The color of this dark glass protected the bottle contents from degradation by light. The solidity of this glass and its impact resistance made it easier to transport. Although the problem of container fragility had been solved, an adequate bottle capping system



Figure 4.18. Steuben Glassware at the Corning Museum, in Tate's *Glass, 5,000 years*, 1991.

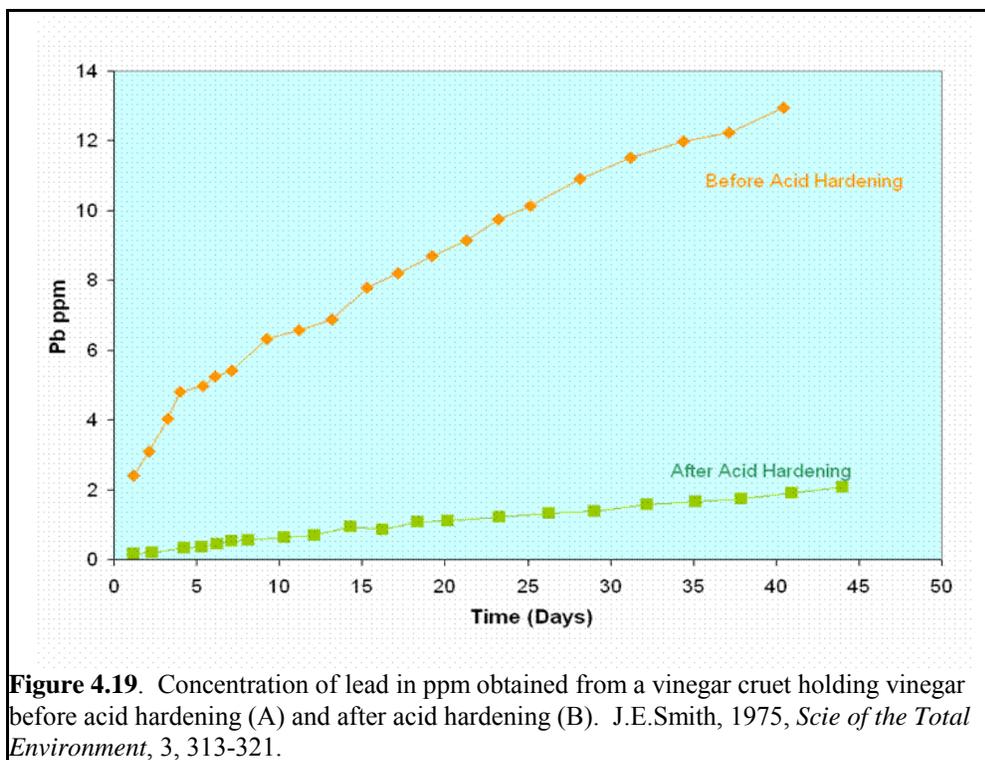


Figure 4.19. Concentration of lead in ppm obtained from a vinegar cruet holding vinegar before acid hardening (A) and after acid hardening (B). J.E.Smith, 1975, *Scie of the Total Environment*, 3, 313-321.

was still needed to exclude oxygen. The use of cork was first mention in 1659. It appears to have developed simultaneously with the impact resistant bottle. Once bottles became sturdy and airtight, wines could be used in export trade (Polak, 1975).

George Ravenscroft (1618-1681 A.D.) participated in the quest for a durable glass. He began by copying Italian leaded glass, known for its brilliance. He was not likely influenced by the work *Ars Vitraria Experimentalis* written by Johann Kunckel (1630-1703), son of the alchemist to Duke Frederick of Holstein. Kunckel's writing incorporated entirely the earlier work of Antonio Neri (1614). Ravenscroft raised the lead content from 10 to 15% (Charleston, 1960). In the stable high heat of the coal furnace, he was able to produce leaded glass. His new glass, patented in 1676, resembled rock crystal.

Leaded glass was used for candlesticks, cruet-sets, punch bowls, and sweetmeat glasses. In 1740 A.D., cutting and engraving techniques for it were introduced to England by German-Bohemians of the Rhine/Rhone glasswork tradition. When cut, leaded glass took on a fine glitter. By 1760 A.D., English glasscutting came into its own. It featured orderly patterns in simple geometrical rhythms. Thickening of the glass made deeper cutting and eventually chandelier

construction possible by the late 1700s. Leaded crystal production took time to become established on the European continent because it had to be coal fired. Several European centers of lead crystal were finally established around 1744 to 1784 A.D.

Figure 4.17 shows an example of Ravenscroft glass. Shown is a colorless lead drinking glass with a chain circuit in relief. Within the stem is embedded a King James II coin from 1687. To the right is a lead glass serving bottle or decanter. Below the neck-ring is an applied seal with a mold-pressed raven's head - a guarantee of George Ravenscroft's improved recipe (Tait, 1991).

The use of leaded glass has continued into this century. Figure 4.22 shows blown glass vases engraved for Steuben Glass Inc (1939-1940) by (left to right) Pavel Tchelitchev, Moise Kisling and John Gates, and Paul Manship.

By 1933 Corning Glass Works had developed a new chemical formula for a colourless lead glass of matchless purity. Steuben Glass Inc. was formed to produce it, and John Gates, the sculptor Sidney Waugh and later others were hired to design the products. As was characteristic of American glass-working in general, the first gaffers and engravers were foreign-

born; in particular, the copper-wheel engravers who adorned the more important examples were often Swedish or Czech. *Tchelitchew's Acrobats* was engraved by Josef Libisch on a large brandy glass shape adapted to the strikingly original design (Tait, 1991).

Toxicity of Leaded Glasses

Should fine table crystal be thrown away because of its lead content? Not necessarily; leaded glass is typically 2.5 to 33% PbO. The lead is network-linked within the glass. The lead cannot be removed unless the glass dissolves in some way. Lead is not known to mobilize from leaded glasses except vinegar cruets in which the vinegar (acetic acid) is stored for extended time periods, allowing etching (dissolving) of the glass surface to occur. The durability of lead oxide-containing glasses depends upon the stability of the lead oxide in various pH solutions. In the binary PbO/SiO₂ system, either the PbO or the SiO₂ will determine solubility at any given pH. Si is relatively more soluble than PbO in alkaline solutions. Consequently, PbO increases the stability of the glass in the alkaline regime (Figure 4.43). The opposite is true under acid conditions. Under acid conditions lead can be leached over time from the glass (Figure 4.19) (Smith, 1975).

Stained Glass

Glass is stained by painting the surface with a lead oxide power base containing various metal oxide colorants. The glass is next baked at a temperature high enough (1300 C) to fuse the oxide powder to the glass substrate. Stained

glass allows the glass artist to create a picture in glass that does not involve cutting of small pieces. Figure 4.20 shows a modern stained glass artist at the Botti Studios of Evanston, Ill in 2002.



Figure 4.20. Stained glass is glass painted with lead oxide based pigments which are then baked onto the substrate glass. This allows greater imagery than purely cut glass. Botti Art Studio, Evanston, Ill., 2002 (Author).

ENAMELS

The Aldrevandin works of Venice (1280-1340 A.D.) used a chemically complex early enameling process (Figure 4.21). This process employed a blue enamel created by mixing lead/tin opacifier with soda/lime glass and cobalt oxide coloring material. The enamel was fused, then crushed, to obtain a material like that of the glass vessel it would coat. The similarity made firing the enamel at its melting temperature difficult since that temperature would also melt the glass vessel. Apparently the vessel was re-supported after painting, during the fusing of the enamel to the glass.

The colors and technology of the glass and enamel were identical to those employed in the Near East, suggesting that both the technology and colorants derived from imported material. The Venetian glass technology grew after the fall of Islam and the carrying

off of Damascus glassmakers to Samarkand by the Mongol Tamerlane in 1400 A.D. (Freestone and Bimson, 1995).

A second enameling process involved the fusing of glass to metal. Theophilus described enamels on metal as recycled Roman mosaics (Dodwell, 1961):

In the ancient buildings of pagans, various kinds of glass are found in the mosaic work - white, black, green, yellow, blue, red, and purple. They are not transparent but are opaque like marble, and are like little square stones. From these enamels are made in gold, silver and copper

Twelfth-century A.D. metal enamels from the River Meuse area of northern Europe are disproportionately high in antimony and Na. Their composition suggests that they re-used Roman glasses (Table E.7 (Freestone, 1992)).

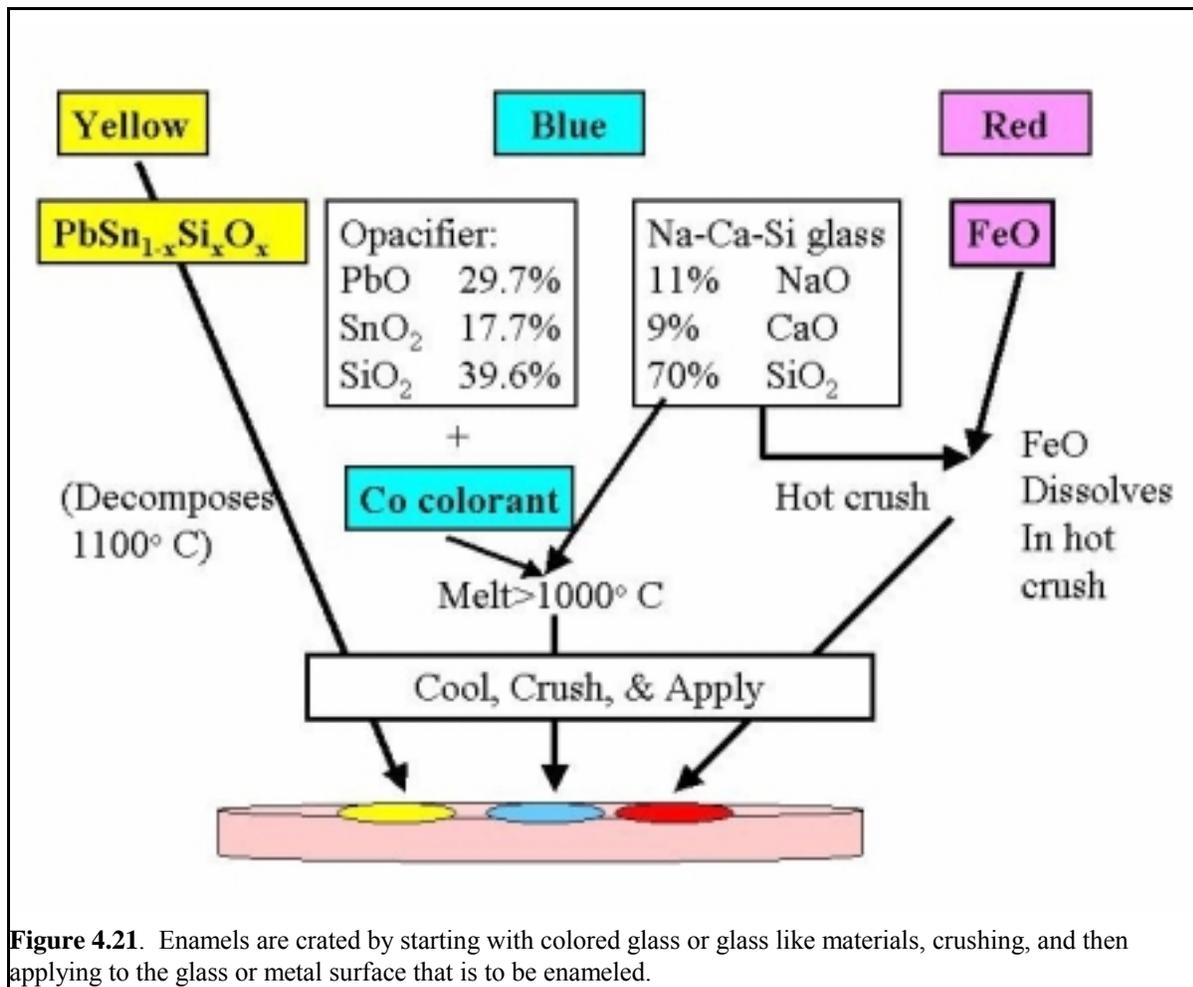


Figure 4.21. Enamels are created by starting with colored glass or glass like materials, crushing, and then applying to the glass or metal surface that is to be enameled.

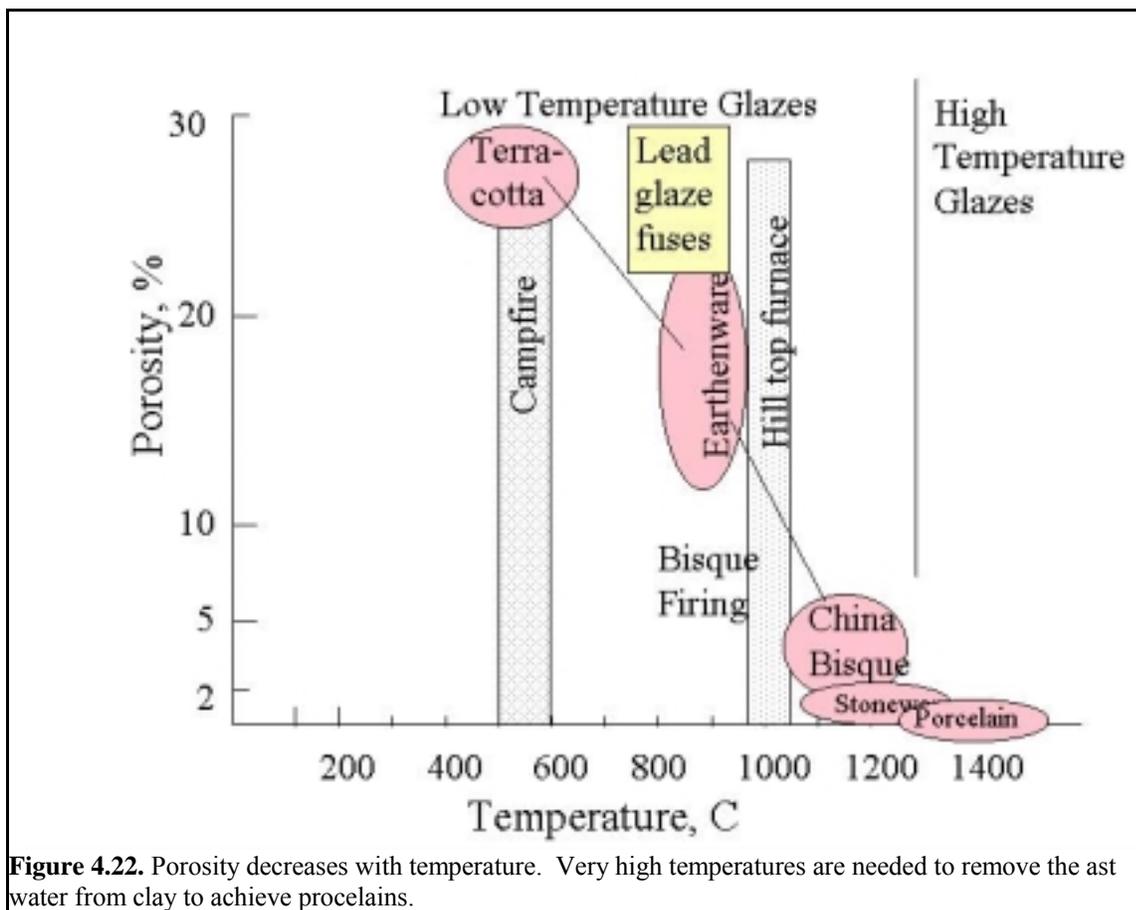
GLAZES

Diffusion of Glaze Technology

The earliest glazes were those the ancient Egyptians applied to faience objects. Faience are high-silica ceramics which held these alkaline glazes well.

Unless a colorant was added these alkaline glazes were transparent. They contained 17-19% Na_2O and 2% K_2O , both water-soluble materials. In order to prevent their solubility, they were burned with silica to create a solid, which was ground and crushed to create a frit and then applied to the object (Tate et al., 1998).

The chief difficulty with alkaline/silicate glaze was its ability to match the expansion and contraction of pottery. Alkaline glazes did not adhere well to pottery. An estimated 99% of ancient clay ceramics were unglazed. The transition to glazed pottery apparently was made possible by lead glazes which had the advantage of matching pots' thermal expansion and contraction, so that the glaze did not crack upon cooling.



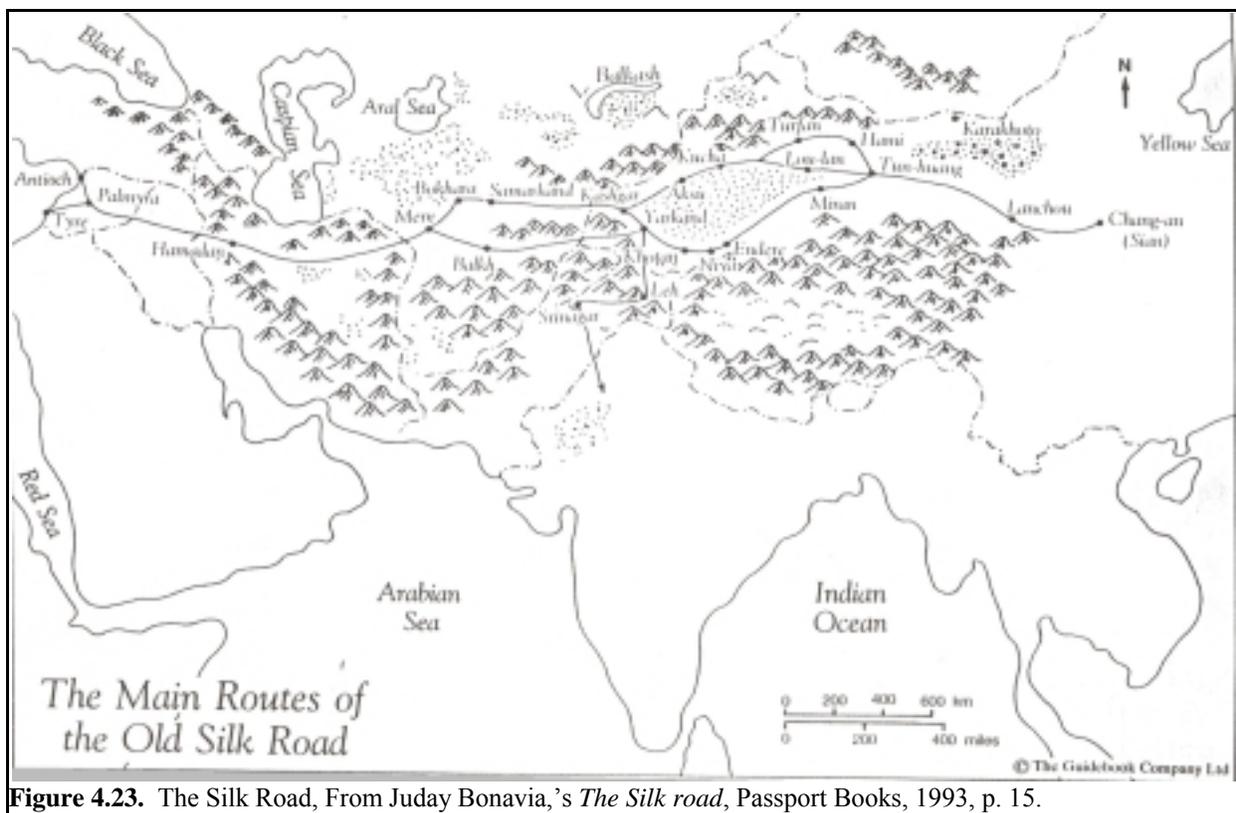


Figure 4.23. The Silk Road, From Juday Bonavia, 's *The Silk road*, Passport Books, 1993, p. 15.

Ashurbanipal's Nineveh library preserved a Babylonian glaze recipe from 800 B.C.:

24.3 parts glass
 40 parts lead
 50 parts copper
 5 parts tin
 3.1 parts salt peter

Despite the early date of this recipe, lead glaze was not widely used in the Middle Eastern/Mediterranean world until the first century B.C. (Hatcher et al., 1994). A study of material from the Louvre and the Ashmolean Museums (problematic since most of it was obtained without provenancing) dated Roman objects stylistically to the first centuries B.C. and A.D.. X-ray fluorescence examination revealed the objects to be uniformly coated with a lead glaze containing 50-80% lead oxide. This composition is consistent with that of other Roman work (Table E.6) (Caley, 1947). The ceramics in the table come from all parts of the Roman Empire. The consistency of the glaze recipe throughout the Roman Empire suggests a standard procedure used throughout the Empire.

Chinese Lead Glaze Early Historical Developments

The Chinese used transparent leadless glaze similar to the western alkaline one, except that it was based on potassium nitrate, which is less soluble than sodium nitrate. Leaded glaze appears in China during the reign of Xuan (73-48 B.C.) and spread quickly. It is not clear if it was contemporaneous with western leaded glazes or independent of them.

The Chinese experimentation with pottery led to some remarkable achievements, including the firing of porcelain. Figure 4.22 shows the types of temperatures required to develop the low-porosity porcelains. Clearly, their development was not a trivial accomplishment. Why did the Chinese achieve such a high level of pottery technology?

The Chinese used bronzes as ornamental and ritual burial objects. Along with these objects, live slaves were buried. Several dozen to several hundred were placed in each tomb during the Western Zhou period (1050-950 B.C.). By 500 B.C., immolated slaves were placed side by side with clay figures ((Vainker, 1991). However, in the simultaneous Eastern Zhou period, live burial was no longer regarded as ritually correct. Mencius (372-289 B.C.), a disciple

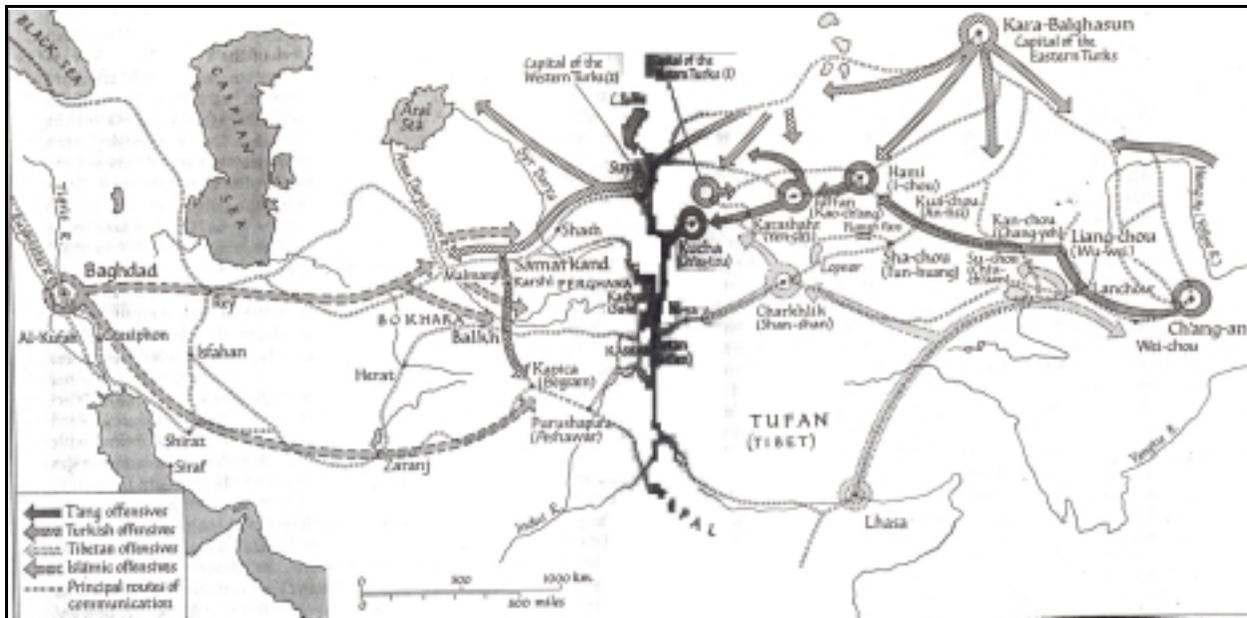


Figure 4.24. The T'ang expansion is shown in the context of other movements of tribes of the times. From Jacques Gerret's *A History of chinese Civilization, 2nd Ed., 1985, p. 254.*

of Confucius, railed against burial of human images. During the wars of 481-221 B.C. the feudal system broke down, allowing many to imitate high life rituals. Cheaper clay products began to imitate the bronze materials previously used in burial. The 1st Yellow Emperor (221-206 B.C.), initiator of the Great Wall, was buried with purely terra cotta figures - 7,000 life-size warriors.

The 1st Yellow Emperor's reign was followed by another troubled period. This period had a liberating effect on ceramics. As long as important ritual objects were constructed from precious materials, ceramics were deemed a stepchild of art. With the breakdown of social order, the lack of precious material, and the use of metals in warfare, ceramics were poised to make inroads on ceremonial objects. Many of these objects were lead-glazed. Tricolor glaze or *sancai*, gave a particularly beautiful effect, as the colors "run" down the side of the vessel.

Potters experimented with shapes as well as glazes. A new shape appeared in the 5th century A.D.: the *bianhu*, or flattened vase or pilgrim flask. It originated in the increasing influence of Westerns moving across the Silk Road (Figure 4.23). The Silk Road became important in recorded Chinese history around 100 B.C., during the reign of the first Yellow Emperor. During this Emperor's reign, the movement of the Mongols pushed Huns out. Some of the Huns

moved south to western China (50,000 families), while the remainder moved west and north to start the age of migrations in Europe.

Sima Qian, in his *Records of the Grand Historian* begins his account as follows (Watson, 1993):

After the Han had sent its envoy to open up communications with the state of Daxia (Bactria), all the barbarians of the distant west craned their necks to the east and longed to catch a glimpse of China. Thus I made "The Account of Dayuan".

...At this time (140-135 B.C.) The emperor questioned various Xiongnu (Huns of Turkish descent.) who had surrendered to the Han and they all reported that the Xiongnu had defeated the king of the Yuezhi people (Indo-Scythians) and made his skull into a drinking vessel. As a result the Yuezhi had fled and bore a constant grudge against the Xiongnu, though as yet they had been unable to find anyone to join them in an attack on their enemy.

The Han at this time was engaged in a concerted effort to destroy the Xiongnu, and therefore, when the emperor heard this, he decided to try to send an envoy to establish relations with the Yuezhi.Zhang Qian set out from Longxi, accompanied by Ganfu, a Xiongnu slave who belonged to a family in Tangyi. They traveled west through the territory of the Xiongnu and were captured by the Xiongnu and taken

before the Shanyu. The Shanyu detained them and refused to let them proceed...

The Xiongnu detained Zhang Qian for over ten years and gave him a wife from their own people, by whom he had a son.He and his party finally managed to escape and resume their journey toward the Yuezhi....

After hastening west for twenty or thirty days, they reached the kingdom of Dayuan. The king of Dayuan had heard of the wealth of the Han empire and wished to establish communication with it, though as yet he had been unable to do so. When he met Zhang Qian he was overjoyed and asked where Zhang Qian wished to go.....

The King of Dayuan trusted his words and sent him on his way, giving him guides and interpreters to take him to the state of Kangju (Trans-Oxiana). From there he was able to make his way to the land of the Great Yuezhi.

Since the king of the Great Yuezhi had been killed by the Xiongnu, his son had succeeded him as ruler and had forced the kingdom of Daxia (Bactria) to recognize his sovereignty. The region he ruled was rich and fertile and seldom troubled by invaders, and the king thought only of his own enjoyment. He considered the Han too far away to bother with and had no particular intention of avenging his father's death by attacking the Xiongnu. From the court of the Yuezhi, Zhang Qian traveled on to the state of Daxia, but in the end he was never able to interest the Yuezhi in his proposals.

After spending a year or so in the area, he began to journey back along the Nanshan or Southern Mountains, intending to re-enter China through the territory of the Qiang barbarians, but he was once more captured by the Xiongnu and detained for over a year.

Just at this time the Shanyu died and the Luli King of the Left attacked the Shanyu's heir and set himself up as the new Shanyu (126 BC). As a result of this the whole Xiongnu nation was in turmoil and Zhang Qian, along with his Xiongnu wife and the former slave Ganfu, was able to escape and return to China. The emperor honoured Zhang Qian with the post of palace counsellor and awarded Ganfu the title "Lord Who Carries Out His Mission"....

Thus the emperor learned of Dayuan, Daxia, Anxi, and the others, all great states rich in unusual products whose people cultivated the land and made their living in much the same way as the Chinese. All these states, he was told, were militarily weak and prized Han goods and wealth. He also learned that to

the north of them lived the Yuezhi and Kangju people who were strong in arms but who could be persuaded by gifts and the prospect of gain to acknowledge allegiance to the Han court. If it were only possible to win over these states by peaceful means, the emperor thought, he could then extend his domain 10,000 li, attract to his court men of strange customs who would come translating and re-translating their languages, and his might would become known to all the lands within the four seas.

Some 20 years later, the Emperor Han Wudi sent 40,000 troops to Ferghana (current-day Uzbekistan) in 102 B.C. to demand horses. The defeat of his army did not deter him. He sent a second army of 60,000 that obtained 3,000 horses (Books, 1993). The first diplomatic exchanges across the silk road to Iran began in 106 B.C. (Watson, 1984).

The effect of Han Wudi's adventure on events in China was momentous, for a way through to the western lands was now known and recorded. Around 100 A.D., Buddhist missionaries began moving across the Silk Road to China. After this Han dynasty, China was beset with the internal turmoil of the Warring States for several centuries. This turmoil unsettled the population and was coincident with incoming ideas. By the end of this unrest, Buddhism was firmly ensconced in Chinese thought. A more peaceful era commenced with the foundation of the T'ang dynasty by Li Yüan (565-635 A.D.), a rebel general of the Sui Dynasty, who made an alliance with Turkish tribes and mounted a coup d'état in 617. The T'ang were able to consolidate power by expanding horse-based warfare. At the beginning the empire had only 5000 horses, but public horse farms raised that number by 650 A.D. to 700,000. Figure 4.24 shows the expansion of the T'ang dynasty westward, beginning in 630 A.D. with the defeat of the Turks. By 662, China was meddling in the internal affairs of states along the Tigris River and setting up puppet states in northern India, Korea, and Vietnam. In 751, the Arabs defeated the Chinese in the battle of the River Talas, south of Lake Balkhash (Gernet, 1997, p. 259). During this battle, Chinese papermakers were carried off to help establish papermaking industries in the Middle East.

T'ang Sancai or Three-Color Glaze

The interplay between East and West is shown by the large camels and bright figures of three-color



Figure 4.26: Group of sancai tomb figures comprising two earth spirits, two devil chasers, and two civil officials. From the tomb of Liu Tingxiu, 728 A.D., In S. J. Vainker's *Chinese Pottery and Porcelain from Prehistory to Present*, 1991, Fig. 59.

(lead) glaze in Chinese funerary art. The making of three-colorwares apparently centered upon three northern kilns: one at Yaozhou near Tongchuan in Shaanxi, another at Neiiu in Hebei, and yet another at Gongxian in Henan. Analysis of these pots at the British Museum have shown that the monochrome and lead-glazed wares were constructed of the same body material and fired at the same temperature. The three-color ware (*sancai*) is created by adding metal oxides to the lead glaze (copper for green and iron for amber or brown).

Figure 4.25 shows a sancai dragon pot. The colored lead glazes have run down the vessel and obscured some of the decorative details.

The tomb figures in sancai are truly remarkable. Figure 4.26 shows a group of sancai tomb figures that includes two earth spirits, two *lokapal* (Sanskrit word for "devil chasers") and two civil officials. The horse, two camels, and several grooms also in the British Museum came from the same group in the tomb of Liu Tingxun, who died in AD 728. Chancellor Liu was a general of the Zhongwu army, a Lieutenant of Henan and Huainan

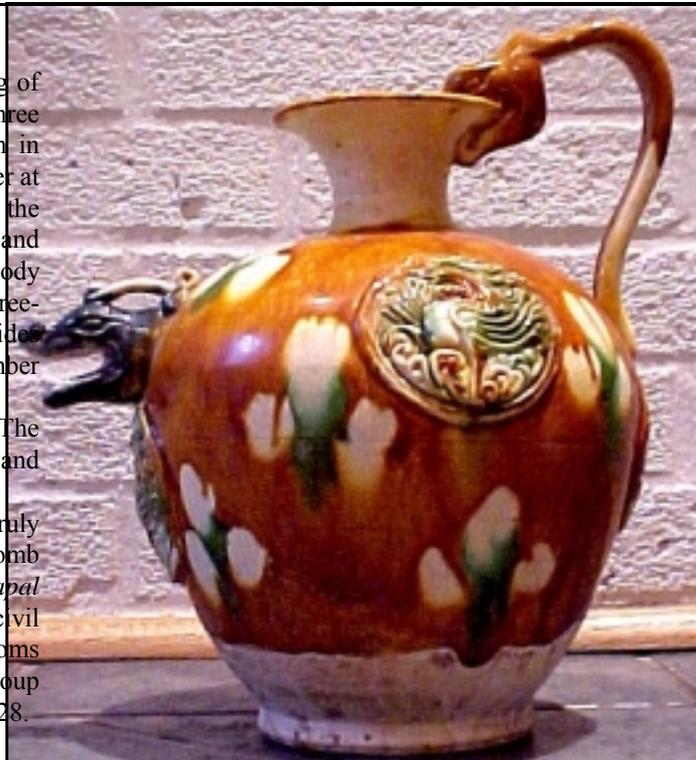


Figure 4.25: Sancai Dragon pot. Hongzhou, 2002. Supposedly from 1850s. (Author).



Figure 4.27 Sancai vase, Hongzhou, 2002, supposedly from early 1800s. (Author).

districts, and a Privy Councillor. The memorial tablet found with these figures records his skill in military matters and the arts of statesmanship, and the fact that he died at the age of seventy-two. These figures are among the tallest extant T'ang burial figures. They form part of the largest group from a single site belonging to a public collection (Vainker, 1991). Notice that the heads were not glazed, but were painted after firing so the glaze would not run. Figure 4.27 shows another example of Chinese lead oxide glaze. This piece is approximately dated to the last dynasty of the 1800s.

Because the use of sancai wares in the north was subject to social restrictions, the presence of glazed figures in tombs is a good indication of the status of both the ceramics and the deceased. Earthenware figures were displayed on carts as part of the funerary procession. Once the procession arrived at the tomb, all the models were lined up outside in the manner of the spirit roads of stone sculptures at the

imperial tombs. When the coffin was placed inside the burial chamber, the figures were moved into the tomb and in their proper positions. Each type of figure had a particular funerary role. For example, a seated beast with a half-human face was intended to frighten away spirits. In addition to these larger and more formal figures there were animal models ranging from the polychrome camels of the Silk Route to small white-glazed domestic animals such as dogs or pigs.

Sancai ware was exported. Pieces have been found in Japan, Southeast Asia, the Middle East, and Africa.

Porcelain and Its Imitation: Iznik Lead/Tin Glaze

During the T'ang dynasty (618-906 A.D.), the exceptional skill of the Chinese potters culminated in the development of porcelain. The use of pottery was accelerated when currency became insufficient for imperial needs. In 713 A.D., an imperial edict prohibited export of currency. In 723 A.D. another decree forbade the manufacture of bronze vessels so that copper could be reserved for money. Internal warfare between 755 and 763 A. D. established the role of the merchant class over the nobles. The confluence of social change, experimentation, and reduced use of metal led to the development of porcelain, a remarkable technical achievement. Kaolin-type clays, which are low in transition metal impurities, are fired at very high temperatures (1400 °C) to fuse them. Firing results in a glass-like translucent ceramic. The fused product has a high refractive index and many scattering centers, and few color-forming sites of transition metals. The results is a white color (Figures 4.28 and 4.29). The low porosity creates a glass-like hardness in the plates.

Major porcelain production in China came to full flower during the Song and Yuan (Mongol) dynasties. However, export of porcelains began around 900 A.D. Muslims in the port town of Quanshour, Fujian Province controlled the marketing of porcelain and throughout the Islamic world. White porcelain with blue cobalt glaze was exported via the Silk Road. It was to have a major impact on the history of lead.

The Silk Road porcelain trade galvanized the relatively new Islamic states. Islamic potters could not reproduce porcelain because they were not working with kaolin clays fired at high temperature. They did invent a white high-luster ceramic called *majolica* through a process of lead-tin glazing. Abu'l Qasim describes the production of tin/lead glaze. Tin glazing is a lead glaze to which tin oxide has been added. SnO_2 is an opacifier. It does not interact with light because

it has a d^{10} configuration. It thus reflects all light and gives a white color. This base is then overcoated with a lead glaze to give additional brilliance.

The presence of the lead produces a brilliance that mimics the translucence of porcelain. The presence of tin oxide produces the white background. In addition, this tin/lead glaze allows for pot production to occur at much lower temperatures. Although pots fired at lower temperatures are more porous, the lead glaze achieves a sealing glassy state at such temperatures (Figure 4.22). Figure 4.30 shows an Isnik Pilgrim's Flask (Figure 4.28) with Isnik lead glaze (Figure 4.29) (Author).



Figure 4.29. Rotation of the eggshell porcelain shows that internal markings can be viewed.

then the Ottoman Turks, ceramic tiles based on tin glazes (Karmason and Stacke, 1989), particularly of the Iznik ware variety from northwest Anatolia were made in large numbers.

Spain and Birth of European Majolica

The technology of lead glazing with tin to produce white ceramics and to seal more porous pots was transferred from the rest of the Islamic world to Islamic Spain (Figure 4.31, Time line J.10) where production was centered near Valencia. The technology was initially used in southern Spain, particularly in Talavera de la Reina (Figure 4.31) The design motif of glazed ware from this area consisted mainly of decorative or moving lines because of Muslim prohibitions on the



Figure 4.30. Pilgrim's Flask with Isnik lead glaze from Yanni Petsopoulos' *Tulips, Arabesques, and Turbans*. The glaze mimics porcelain.



Figure 4.31. Talavera ware (Barcelona, Spain, 1999, leadless), carries the Islamic tradition of blue on white background with no human images. Added was a characteristic raised dimension. (Author).

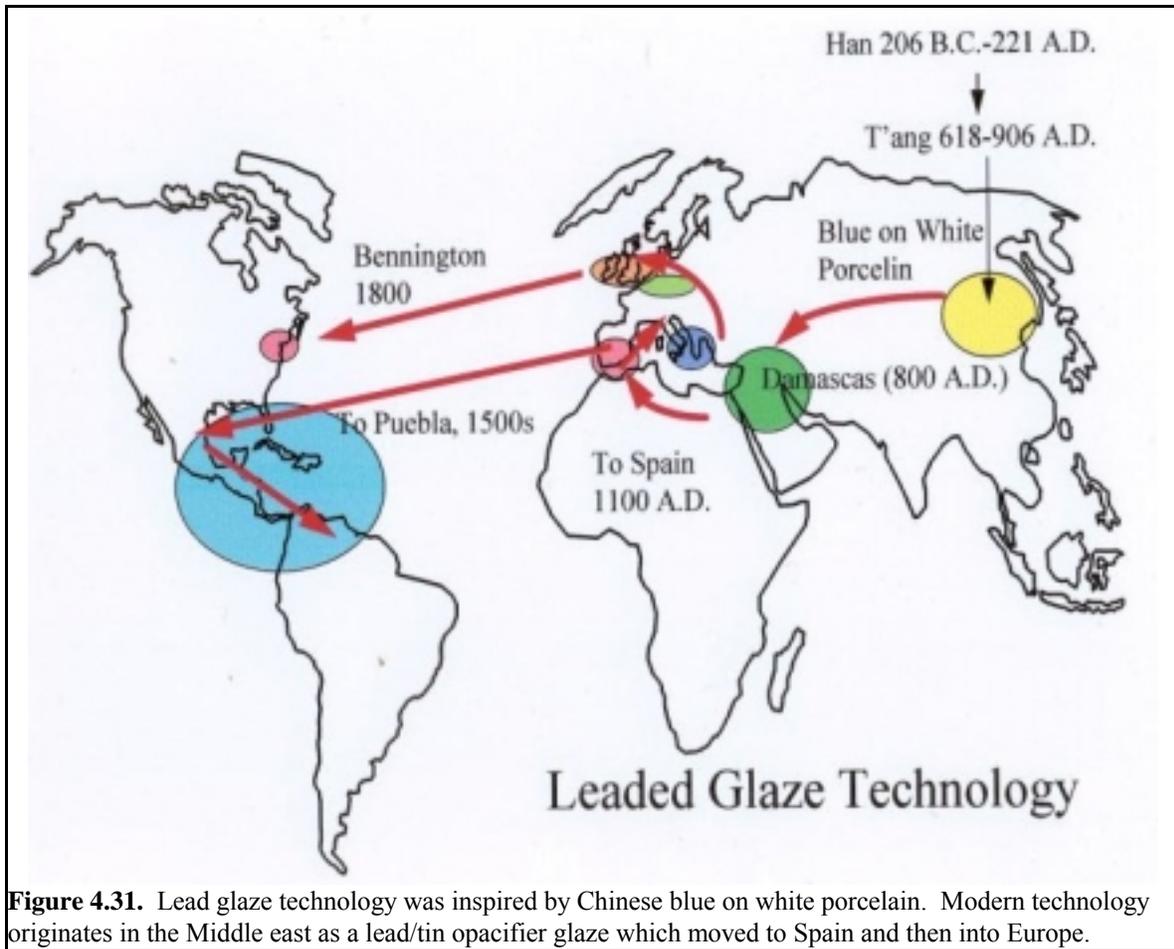


Figure 4.31. Lead glaze technology was inspired by Chinese blue on white porcelain. Modern technology originates in the Middle east as a lead/tin opacifier glaze which moved to Spain and then into Europe.

use of figures. The traditional blue and white Spanish work, derived originally from Chinese porcelains, found its way into Spanish tile work. The glaze was exported through the island of Majorca from which it derived its Italian name of maiolica.

The export of this glaze coincided with the weakening of the strict guild system in Europe. When the guild system waned, pottery artists joined with painters to develop a style of painted figure-based pottery called *majolica* or *maiolica*, meaning “derived from Majorca”. This huge change in style moved pottery from the bottom of the European taste scale to its top. Major production centers were Florence, Urbano, Siena, Faenza, and Castel Durantino.

During the Italian renaissance tin/lead glaze took its name from the city of Faenza, where the modern style of pottery began. Around 1477, Faenza pottery styles began to change. Religious figure motifs

began around the edge of the plates. Florentine potters began to incorporate figures in the mid-15th century, using the skills of the greatest contemporary painters. Over the next century there was a lively experimentation with visual images and styles, as well as allegorical images. Maiolica production in Italy likely crested by the end of the 16th century, while French and Dutch production began to increase. Classical Italian maiolica was described by Cipaino Michele di Piccolpasso (1524-1579 A.D.) from the province of Pesaro e Urbino. He wrote the earliest known manuscript on pottery *Li tre libri dell'arte del vasaio*.

Italian maiolica in turn influenced glaze production back in Spain, this time in the city of Talavera.

The transfer of lead glaze technology across Europe occurred by migration, theft, and family dynasty. Figure 4.33 the rapid spread of leaded glazes throughout Europe and the major production centers in



Figure 4.35. Bernard Palissy (1550-1570) oval dish with high relief. From Giuseppe Scavizzi's *Maiolica, Delft, and Faience*, 1970, plate 27.

In addition to developing a white glaze, Palissy worked with raised detail, or three-dimensional art, on the pottery surfaces. The raised effect is shown in the Palissy oval dish Figure 4.35 (Scavizzi, 1970). He decorated the Tuileries grotto for Catherine de Medici. Scavizzi characterizes it as surrealistic and slightly repellent in effect.

Germany was also the recipient of Italian technology. Hirschvogel of Germany visited Italy in 1503 and carried back a recipe of majolica (Parmalee, 1973). Guido Andries of Castel Durante immigrated in 1512 to Antwerp where he established a pottery. His son, Jaspas Andries, and the son's partner, Jacob Jansson moved in 1571 to England where they set up shop in Aldgate London. This first move across the channel was followed by several more waves, primarily in 1650 and 1689 accompanying the ascension of William of Orange to the English throne. One set of Dutchmen, Daniel and John Elers, moved to England in 1684 where they worked first in the firm of John Dwight, a stoneware potter in the London area. In 1693 Dwight sued the two Elers and three members of

the Wedgwood family for infringing on his patent rights when they set up shop in the Staffordshire area. The Elers, mindful of the risks of losing trade secrets themselves, employed only the "weak of mind" in their shop. This did not stop John Astbury from posing as an idiot to obtain recipes for pots and glazes. Astbury then set up his own shop in 1730. It is in Astbury's shop that the lead glazed creamware was developed. Astbury was, in turn, the mentor of Thomas Whieldon, who, in turn, was the mentor of Josiah Wedgwood and Josiah Spode. The lead glazed creamware of Astbury was refined by Wedgwood to become the stylish and popular Queensware. The Wedgwood firm later shared technology with the Minton firm. The Minton firm got its start with Thomas Minton who designed for Josiah Spode. His son, Herbert Minton, resurrected the three dimensional styling and coloring of the Italian maiolica which they termed "majolica" (Karmason and Stacke, 1989), (Snyder and Bockol, 1994).

By 1851, there were 1130 English firms specializing in majolica. Most of them were in Staffordshire, thus the term "Staffordshire" became a



Figure 4.36. German Majolica, early 1900s or late 1800s. Purchases, Wilmette, IL., 2002. (Author).



Figure 4.38. English yellow ware cradle, early 1800s. Purchased, Cambridge, England, 1999 (Author).

synonym for “majolica”. Prominent workers in the area included W. T. Copeland (1847), George Jones and Sons (Stoke-on-Trent, 1861), Herbert Minton, and Minton’s apprentice Joseph Holdcroft. Wedgwood entered the market in 1862 by hiring Minton’s designers.

Back in the Netherlands, workshops were concentrated in Delft: hence the term Delftware. In the mid-seventeenth century, Delft breweries declined due to competition from England where glass bottles and exports had made brewing very lucrative. The Delft breweries shifted to majolica production. Ceramic manufacturers retained the old brewery names, such as Three Golden Ash-Barrels and the Golden Jug. Workers in this area concentrated on mythology and landscapes. Figure 4.36 shows an early 1900s, late 1800s German majolica vase. Note the similar brilliance, texture and color selection to the earlier piece by Palissy.

The tradition of lead/tin glaze moved with the lowland Dutch to England with the ascent of William of Orange. The English potter Herbert Minton, influenced by Palissy’s work, gave the English trade name to the glaze majolica (Snyder and Bockol, 1994).

The brilliant yellow of lead antimonate which disappeared from



Figure 4.37. 1802 English Yellow Ware jug, probably Thomas Harly, Lanes End pottery. From Jefferson Miller II’s *English Yellow Ware*, 1974, p. 57. Smithsonian Institution Press



Figure 4.39: A Griffin majolica bowl. A bowl of this make was discovered under the childhood home of the author's mother.

glasswork at the end of the Roman Empire (Figure 4.1) when silver mining declined reappeared as Naples Yellow in painting (see next chapter) and as English Yellow ware (Miller, 1974) (Table F.13). The pot in Figure 5.37 is dated to 1802-5 from Thomas Harley's pottery in Lane End, it is a jug with diamond-quilted relief pattern painted with silver luster. The toy cradle in Figure 5.38 is dated to 1810-1820. Most yellow cradles have incised and Rockingham decorations. They were originally made as christening gifts between 1810-1830 in England (McAllister, 1997).

Lead Glazed Pottery in the U.S.

The tradition of English Yellow ware moved to the United States in the first half of the 1800s. James Bennet, of Derbyshire England, a Yellow Ware potter moved to the United States in 1834 where he worked at the Jersey City Pottery in Bergen, N.J. Three years later he moved west to the Indiana Pottery Co. located in Troy where he worked on white ware. The following year he traveled up the Ohio river and on the journey he noticed clay on the banks of the Ohio

river that would serve as a basis for a new industry. In 1840 he built a 20 by 40 foot pottery with one kiln at East Liverpoole, Pennsylvania. The following year his brothers Daniel, Edwin, and William joined him (Karmason and Stacke, 1989). Their major product was yellow ware. Rockingham ware, developed in the early 1800s in England, was also produced. Rockingham ware, a yellow ware, was finished with a brilliant, purple-brown lead glaze colored with manganese.

In 1844 the pottery moved to Birmingham (Pittsburgh) Pa. The goods from this pottery were traded up and down the Ohio River. In 1846 Edwin Bennett moved to Baltimore where he was joined by William in 1848 to form the W. E. Bennett Co. which operated until 1856. In 1850 this firm made the first set of American Majolica.

The original Bennett business on the banks of the Ohio was joined by Anthony Kearns, Benjamin Harken, George Thomas, and George Hollingsworth. Harken shortly set up his own shop in East Liverpoole with James Taylor and Henry Speiler. These latter two later moved to Trenton, N. J. to begin work with leaded

glazed pottery. The original Bennet firm also employed Isaac Knowles. Knowles then branched out on his own in 1853 to set up the firm of Knowles, Taylor, and Knowles.

The many potters in the area resulted in an influx of more potters. Homer and Shakespeare Laughlin moved from New York to East Liverpoole where they built a factory devoted to the production of white ware. In 1936 the Laughlin firm introduced the very popular lead glazed Fiesta ware, which was primarily produced at the New York site of the pottery. Fiesta ware was phased out in 1972, but re-introduced in 1986. It has been lead free since 1992 [Library, 2002 #1993], [AP, 2002 #1994].

A major form of American Majolica is Griffen ware. This company began as the Phoenix Pottery, Kaolin and Fire Brick company May 7, 1867 in Phonenixville, Pa. as a partnership between W. A. H. Schreiber and John Griffen to produce Rockingham ware. Thirteen years later it became Griffen, Smith, and Hill which concentrated on the production of majolica. An example of Giffen ware is shown in Figure.4.39. This piece of pottery was found under the home of the author's mother in the 1933 when the house was cut in half and moved to the town of Riverside, Ca.

Lead Glazed Pottery In Mexico

The 1521 Spanish conquest of the Aztec Empire tremendously impacted lead glazes in the New World. Spanish New World majolica was an item of status and wealth. It apparently was not used by the indigenous people, but was produced for the conquerors, at least until the 18th century. It was found commonly in sites where the clergy, government officials, and wealthy persons lived. The 1679 Spanish export laws regulating trade with the New World clearly preferred the potters of Seville, although Talavera ware was also exported to the goods-hungry New World. Records from about 1540 and again about 1560 indicate that Talavera was exported to the Indies. Such exports continued through the 16th and 17th centuries. Then New World industry began to compete. It was apparently established in production shortly after the conquest, particularly in the large town of Puebla, Mexico. By 1653, various ordinances regulated the distinction between three classes of pottery produced in Puebla: fine, common, and yellow (Goggin, 1968). Majolica production centers were established on a lesser scale in other Mexican



Figure 4.40. Terracotta pots are stacked on a fuel pile in Oaxaca, Mexico, for a low temperature firing of lead glaze. 2002.

Image source:

<http://criticalceramics.org/articles/oax.htm>

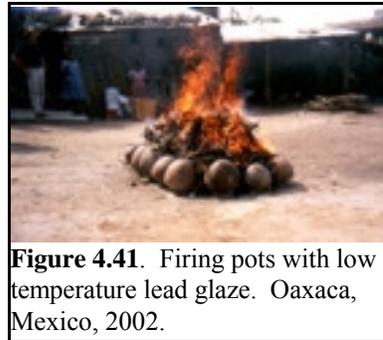


Figure 4.41. Firing pots with low temperature lead glaze. Oaxaca, Mexico, 2002.



Figure 4.42. High gloss lead glaze on terra cotta coffee cup. Mexico, 1997 (Author).

communities: Mexico City, Guanajuato, Guadalajara, Oaxaca, Aguascalientes, Atlixco, and Patzcuareo. According to archaeological evidence, New World productions began to outstrip Spanish exports about

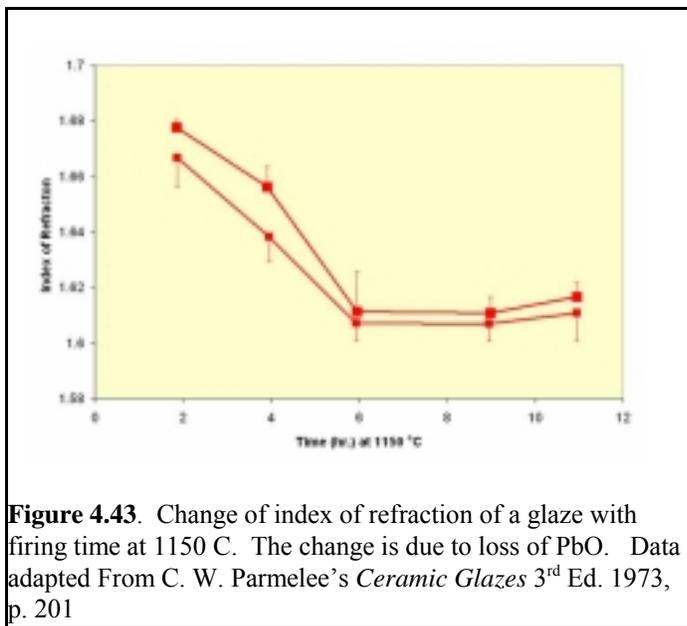


Figure 4.43. Change of index of refraction of a glaze with firing time at 1150 C. The change is due to loss of PbO. Data adapted From C. W. Parmelee's *Ceramic Glazes* 3rd Ed. 1973, p. 201

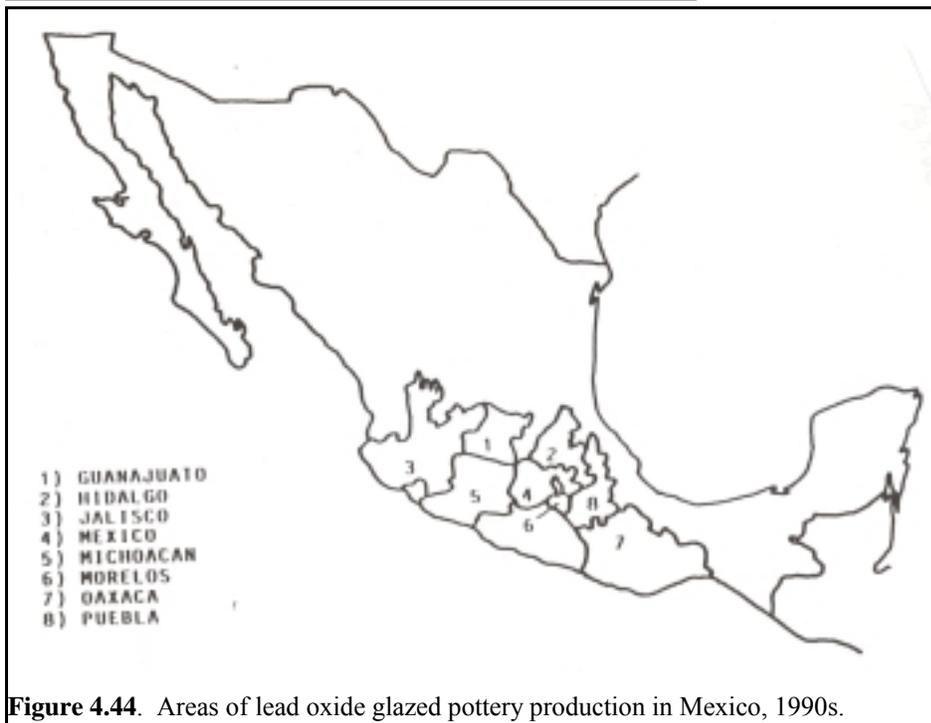


Figure 4.44. Areas of lead oxide glazed pottery production in Mexico, 1990s.

1564 and 1566. Mexico-bound fleets swung northwest to pass Puerto Rico, stopped at the Bay of Neiba in Hispaniola, then went on to Veracruz. After Veracruz, the fleets made for the Florida Straits to catch the winds back to Spain. Majolica trade from Mexico has been found in Florida. After chocolate production was industrialized in Venezuela, ship routes shifted from Mexico to Venezuela, but still carried Puebla and Jalapa majolica.

Lead glazed ceramics in Mexico are pervasive, not only because of the brilliance of the glaze, but more importantly because of the simplicity of the firing process. Figures 4.40 and 4.41 show a typical open firing of pots in the state of Oaxaca, Mexico. Lead glazed ceramics can be fired in open fires at low temperatures. Despite the low firing temperature low porosity is achieved by the sealing action of the lead glaze.

Figure 4.42 shows an example of Mexican lead glazed coffee cup from the state of Puebla purchased in the 1970s.. Puebla remained a major center for majolica throughout the nineteenth century (Sayer, 1990).

Leaded Glaze Frits

One important factor in lead glaze chemistry is the need to prevent gaseous loss of lead. Prevention of lead loss keeps the glaze brilliant. A glaze's index of refraction (the source of reflection) can decrease with time if the lead is not stabilized (Figure 4.43).

Loss of lead as either PbO or as Pb metal vapor is diminished by the addition of SiO₂ to the glaze. Normally, before it is put into the glaze, PbO is first combined with SiO₂ to make what is called a frit. A frit has the additional advantage of reducing the potters exposure to lead fumes.

Exposure to leaded glazes has been well-documented in Mexican pottery works By volume,

1620. By 1650-1660, Spanish Talavera ware was completely eclipsed by Mexican exports to the Caribbean area.

Trade during the early 16th century was not well regulated, but by 1543 A. D., laws required trading fleets to sail during specific periods. Fleet sailing patterns were set by regulations dating between

Mexico is the fifth largest producer of ceramics in the world. These ceramics generally are made by family-owned shops dispersed through out the states of Guanajuato, Hidalgo, Jalisco, Mexico, Michoacan, Morelos, Oaxaca, and Puebla (where it was established by the Spaniards) (Figure 4.44) (Albert and Badillo, 1991). An estimated 100,000 workers are exposed to a high amount of lead during production (Molina et al., 1981; Molina et al., 1980; Molina et al., 1982). Table G.12 shows the average blood lead levels of two groups pottery workers, those working with lead glazes and those not.

Toxicity of Leaded Glazes

Unless the leaded glaze is fired at a temperature that will fuse the lead oxide (~800-900 C) which is above a normal fire of 500-600 C) (Figure 4.22), the lead in the glaze may be unstable. Consequently many small rural operations that fire pots in a normal bonfire may prove to have unstable glazes (Molina et al., 1981; Molina et al., 1980; Molina et al., 1982).

The earliest warning about lead glazes apparently surfaced in England during the 1700s (Meiklejohn, 1954). In 1753, Lind published his *Treatise on Scurvy* which linked scurvy, the debilitating disease of sailors isolated for extended periods of time on boats, to the lack of citric acids in the diet. In 1754 he contributed an article to the *Scots Magazine* concerning the production of fresh fruit juices to prevent scurvy.

I received the following information from a gentleman in London:

“That, intending to make the extracts of lemons, he squeezed the juice of a thousand lemons into a large glazed coarse earthen vessel, and allowed it to stand for two days: he then poured off an English gallon of the clear juice into another glazed flat earthen vessel, and put in in a pot of boiling water to evaporate. During the evaporation, a great quantity of sediment appeared among it, which, upon examination, he found to be the salt or sugar of lead, to the quantity of several ounces. He then poured off the remaining part of the juice of the first earthen vessel, which had not been put upon the fire, and was surprised to find the sides and bottom of it also loaded with a large proportion of the same sort of salt.

This salt was presumed by Lind to be acetate



Figure 4.45. Mexican bean pot, 1970s, is constructed to give an even heat distribution for simmering over a wood fire. It is only partially glazed. (Author).

or sugar of lead, from which he concluded that one should use specific types of glazed vessels:

The most proper vessels for preparing the inspissated juice of lemons, oranges or any other acid fruits, are, first, porcelane, or china ware. The substance of these is of so close a texture, that no saline or other liquor can penetrate them. The glazing which is made likewise of the substance of the china is so firm and close, that no salt or saline substance can have the least effect upon it.

Dr. Gouldson of Liverpool published a pamphlet entitled *Earthenwares Glazed with Lead*. Wedgewood (1773) was aware of these pamphlets and concerned that

When ignorant people read an account of lead and poison and Queen’s ware in the same paragraph they might associate the ideas together....and never after see one of our plates without the idea of being poisoned by it.....I will try in earnest to make a glaze without lead, and if I succeed will certainly advertise it.

Lead glazes can be a rare but acute source of



Figure 4.46 Image from public health poster *Peligros de Plomo* produced by the National Council of La Raza and the National Safety Council. The circled pot is a lead glazed casserole pot. The circled jars on the shelf are home remedies Greta or Azarcón which contain lead.

lead poisoning. A medical report in 2002 described a woman who presented with a four month history of colic-like abdominal pain, hypertomis and anemia, and a 16 kg weight loss over 6 months (Ziegler et al., 2002). The differential diagnosis was hepatitis, Gilbert's disease, anorexia nervosa. She developed intermittent hypertonia and tachycardia. She reported drinking 2 liters of lemon tea a day from a Slovakian ceramic mug. The mug when treated with 10 mL of dilute nitric acid for two hours liberated 1.27 g/L of lead. Her blood lead level was 91.9 $\mu\text{g}/\text{dL}$. A similar case was report in which lead was leached from a glaze by the repeated brewing of tea with its acidic tannins in a ceramic pot (Phan et al., 1998).

While most cases of childhood lead poisoning

are attributed to leaded paint dust within the home, leaded glazes also play a significant role among some populations. In San Diego, California, the Department of Public Health found that 1/3 of Hispanic children identified with asymptomatic lead poisoning were exposed to lead through beans cooked in lead-glazed Mexican pottery. The traditional or rural Mexican diet consists of dried corn soaked overnight with some calcium carbonate (a calcium source) and then ground for tortilla, a flat bread, the next day. The tortillas are eaten with beans (a protein source) that have been soaked overnight and then cooked in a special bean pot designed to distribute heat evenly over a fire hearth. The beans and bean broth are scooped up with the tortilla and eaten with a chili pepper sauce (a vitamin C source).

According to replicate measurements, the lead value of beans cooked in new bean pots (Figure 4.45) was $22.0 \pm 3.4 \mu\text{g Pb/g}$ beans. The value declined over 20 uses to $12 \mu\text{g Pb/g}$ beans. When this amount of lead is added to the EPA total uptake model (soil, air, dust, water), there is a positive correlation between predicted and measured blood lead. This correlation does not hold when the lead from the bean source is taken away (Gersberg

et al., 1997). Similarly, a study of 200 Mexico City women found that lead glaze was the most important determinant of blood lead levels (Hernandez-Avila et al., 1991), as it was for 113 children in Mexico City (Jimenez et al., 1993). The same pattern was shown in a study of 98 women from rural Mexico (Rojas-Lopez et al., 1994).

Figure 4.46 shows an image used on a public health poster *Peligros de Plomo* (Dangers of Lead) by the National Council of La Raza and the National Safety Council. The circled pot is a typical bean or casserole pot and the circled materials on the shelf are for Greta or Azarcón, home remedies (see Chapter 6).

Part II: Chemistry of Glasses and Glazes

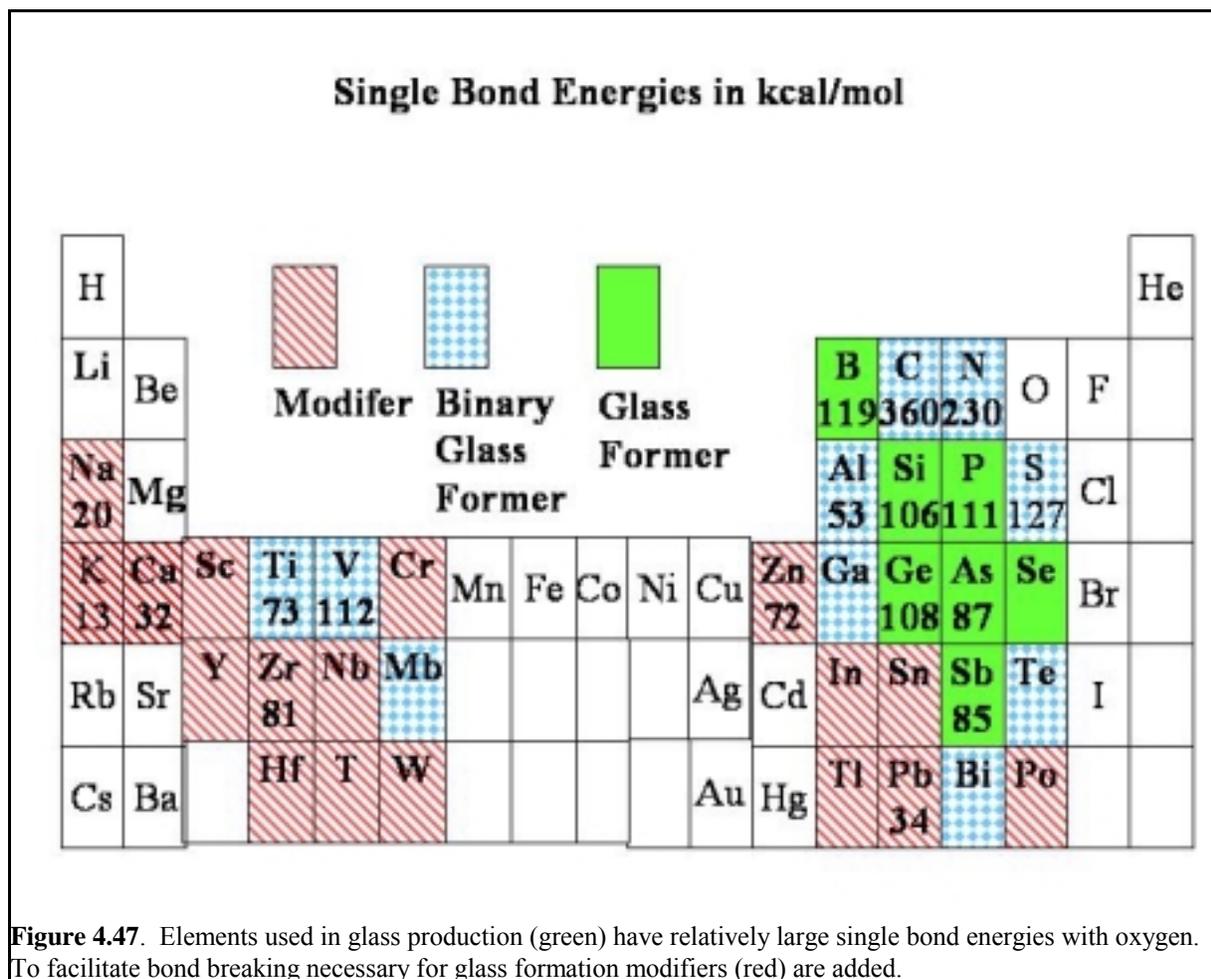
Why Lead and Glass?

What about lead chemistry makes it such a desirable additive to glasses?

Glasses represent a phase of matter between solid and liquid. Glasses are essentially supercooled liquids. Gases are a completely random distribution of molecules. Liquids and glasses are partially random, and solids are organized layers. Motion in a liquid or glass is easier than in a solid because the forces holding the crystal together are not present. The material can flow. Unlike liquids, however, glasses are elastic; once deformed, they can bend back. They are cohesive in contrast to liquids. Nearly all materials can be cooled

from a liquid to a glass state if they are cooled rapidly enough to prevent nucleation sites for crystal growth (Paul, 1990).

A few materials easily form glasses. These are the oxides in which a cation, A, forms an oxide bond with oxygen to create the structure A_xO_y . These compounds are B_2O_3 , SiO_2 , GeO_2 and P_2O_5 , As_2O_3 , and Sb_2O_3 . A look at the periodic table shows that the useful cations lie just above the non-transition metals (Figure 4.47) and have similar ionic radii, R_A (Figure 4.48). According to one hypothesis, glass-forming oxides are those in which the cation radius, compared to the oxygen radius, R_A/R_o , lies in the range of 0.2 to 0.4. This hypothesis predicts a coordination number of four and thus the development of tetrahedrons



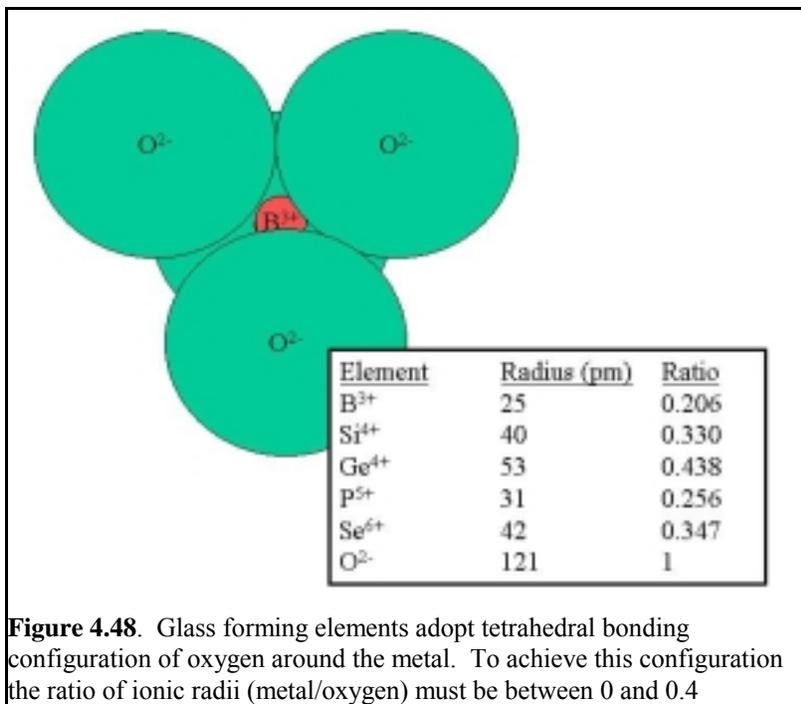


Figure 4.48. Glass forming elements adopt tetrahedral bonding configuration of oxygen around the metal. To achieve this configuration the ratio of ionic radii (metal/oxygen) must be between 0 and 0.4

(Figure 1.49), which are conducive to three-dimensional network formation (Zarzycki, 1991). Among the tetrahedral network formers is SiO₂, the basis of quartz.

What is the difference in bonding between a crystalline solid like quartz and glass? The network in quartz is three-dimensional and rigidly linked; the glass network is more distorted (Figure 4.48). In glass, the polyhedra can share only corners, not edges or faces. This is because oxygen can be linked to more than two atoms of A. Consequently, cations that easily form

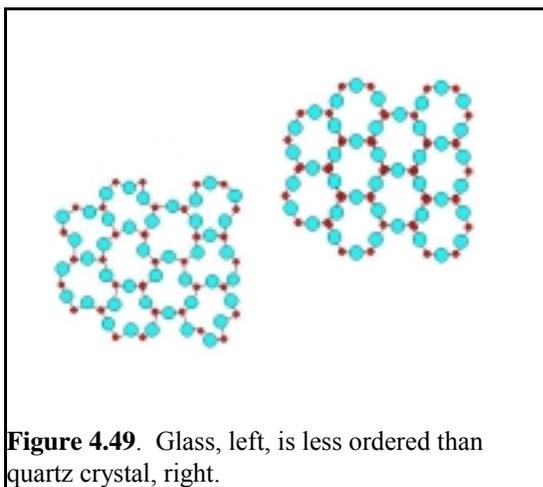


Figure 4.49. Glass, left, is less ordered than quartz crystal, right.

glasses must have bonds with oxygen that are intermediate between covalent and ionic. Purely covalent bonds have well-defined bond lengths, as well as angles more consistent with crystalline structures. Purely ionic or metallic bonds have no directionality in the slippage plane. Intermediate oxygen metal bond energies occur near the end of the d block (Figure 4.47).

In a series of tetrahedra connected only at the corners, the apical oxygen atoms with lone electron pairs can be stabilized by other modifying polyhedra chains or cations (Figure 4.48, and 4.2) (Zarzycki, 1991). The final glass state contains a mixture of chains, rather like a tangle of spaghetti strings. The modifier needs to have properties similar to the glass former, but it must have a smaller covalent bond strength.

For a series of chains connected only at the corner and not at the apex, during cooling of the melt two processes may occur. The chains can be brought to a stable state (cessation of motion) or we can break the bonds at the apices and reform a more rigid matrix (crystallize) starting at nucleation sites (Muller et al., 1993). The rate crystallization rate is related to the breaking of a bond in the tetrahedra. The stronger the bond in the tetrahedra, the more slowly the bonds will break, and the more slowly crystallization occurs. Thus it is not surprising that the species that easily form glasses occupy the position in the periodic table that they do. Close in size and electronegativity to oxygen, they have relatively high bond energies (Figure 4.47, Tables D.16 and D.1).

Flux: K vs Na glasses

Medieval European glasses contained calcium and potassium in addition to silica (Table E.5). These basic contents are also noted in historical accounts from the period. Venetian workers used a soda glass, that is, one made with sodium ash. The glassmakers of Northern Europe used potash, in which the ashes were derived from beech wood, which is high in K and Ca (Table C.10 and C.11). Theophilus gives a recipe for the latter glass. Most of the Northern and Western European medieval glass was made of potash-lime-silica (Cox and Gillies, 1988). The compositions of

various glasses are given in Table E.5, which shows the K content (Freestone, 1992).

On the other hand, opaque (non-transmitting) glasses from northern medieval Europe contained a

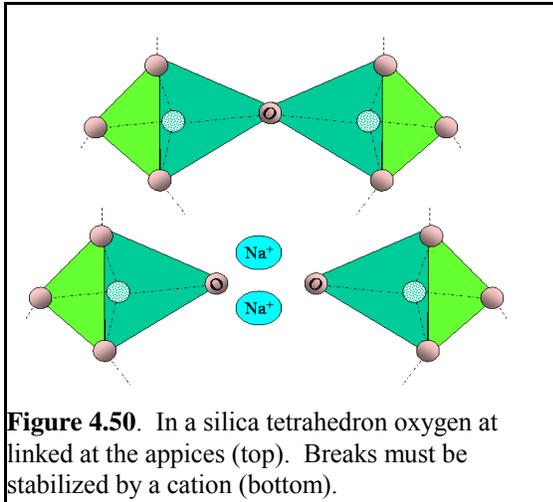


Figure 4.50. In a silica tetrahedron oxygen at linked at the apices (top). Breaks must be stabilized by a cation (bottom).

large amount of sodium, suggesting that they were made from recycled Roman material. This idea is feasible because Theophilus gives glass recipes calling for the use of “Pagan colored stones” (Roman glass).

What was the role of potassium or sodium in glass? In alkali (Li or Na) silicate glasses, modifiers depolymerize the Si-O three dimensional network. This depolymerization occurs because bonds cannot form at the apices of the Si-O tetrahedron without loss of the fluidity necessary for a glass (Bessada et al., 1994). Early glazes were often formed from ashes, a source of either potassium or sodium, both of which can inhibit the glass chain rupture. K and Na impart different properties to the glass. The volume of the glass is larger for K, a larger atom, than for Na. Conversely Na gives a denser glass at temperatures above 25 °C (Figures 4.50 and 4.51). The effect of density for Na fails to counteract the effect of K’s larger number of electrons and the smaller effect that K has on the polarizability of the electrons. Thus K glasses generally have higher refractive indices and reflectivity (Table F.16)

Because Na has a smaller ionic radius and

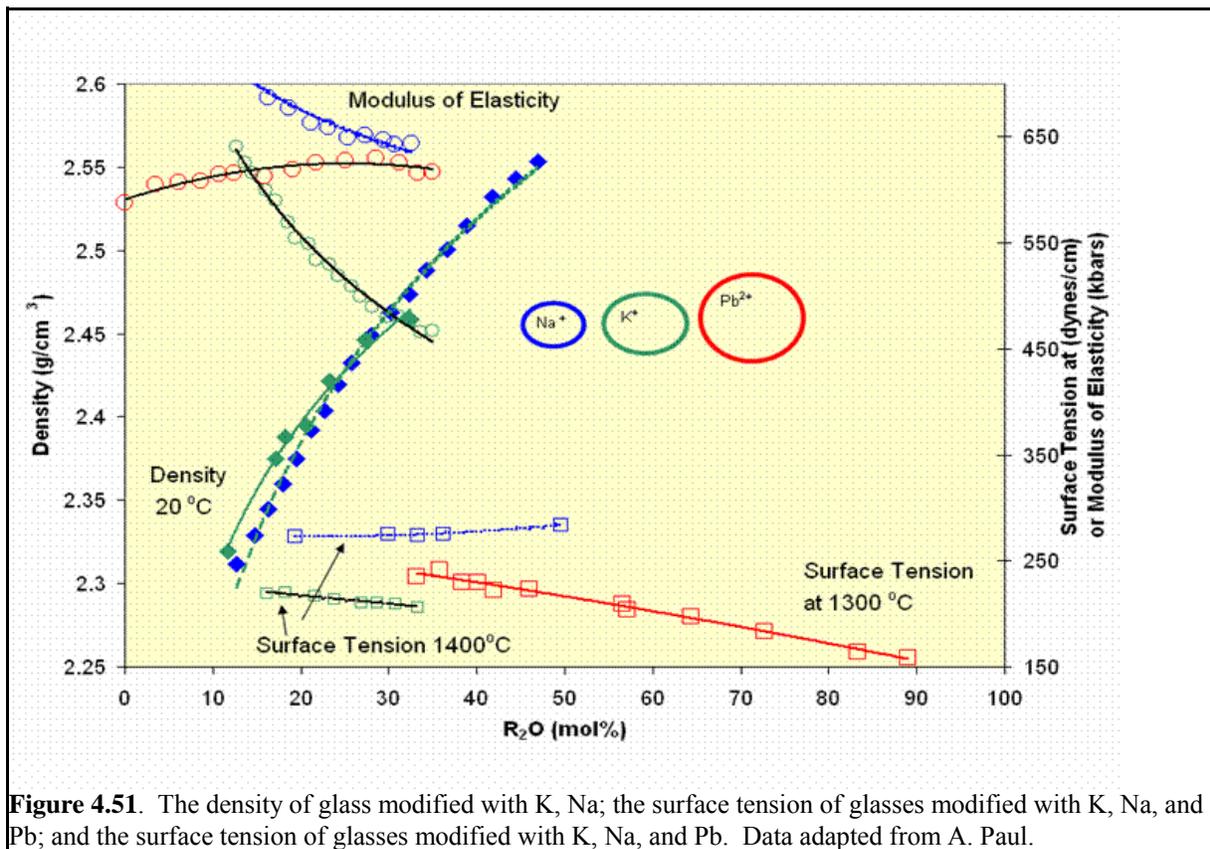


Figure 4.51. The density of glass modified with K, Na; the surface tension of glasses modified with K, Na, and Pb; and the surface tension of glasses modified with K, Na, and Pb. Data adapted from A. Paul.

higher charge density, sodium glasses tend to have a higher surface tension. Thus they are both harder to break and harder to crack. The strength of the glass is described by the following equation:

$$[4.1] \quad \text{strength} = \sqrt{2\varepsilon\gamma/d}$$

where ε is the modulus of elasticity, γ is the surface tension, and d is the crack depth on the glass (Paul, 1990, p. 123). Figure 4.51 gives the modulus of elasticity for various glasses (Paul, 1990, p. 151). Sodium glass has both a higher modulus of elasticity than potassium. The relative strength of sodium to potassium glass at 20% oxide content is calculated to be $\sqrt{3.25}$. This increase in strength gave the Venetian glassmakers an enormous edge over their northern counterparts.

Lead and Flux

Lead resembles sodium and potassium in that its ability to act as a modifier comes from its ability to disrupt the SiO three dimensional structure into two dimensions. When PbO is present in low amounts, the lead primary functions as a charge satisfier for the non-bridging oxygen in the silica backbone (Figure 4.2). Pb^{2+} acts like K^+ or Na^+ to stabilize Si chain breakage.

Lead chains can arise from α PbO (red lead, with a tetragonal pyramidal structure, Figure 4.52) with equidistant (2.31 Å) Pb-O bonds or it can come from β PbO (orthorhombic structure, Figure 4.53) in which two bonds are shorter as if they were covalent (Adams, 1985; Adams and Stevens, 1977; Wells, 1984). Some studies suggest that the red PbO structure predominates in lead chains (Imaoka et al., 1986). Lead can also be present as Pb_2O_4 (Figure 4.54) (Wells, 1984), minium, which contains Pb^{4+} coordinated to two oxygen via covalent bonds and to one oxygen via acceptance of a lone pair electron from that oxygen. Pb_3O_4 also contains tetravalent lead, which is in an octahedral coordination sphere surrounded by six oxygen (Lottici et al., 1991).

Depending upon the mix of lead, the predominating chains can be SiO_4 or PbO (Damodaran et al., 1990). In one study of silicate mixtures, the amount of lead oxides was varied systematically. The volume of the unit cell was found to expand (breaking rigidity) (Stemmermann and Pollmann, 1993) (Figure 4.55) (Stemmermann et al., 1991). The glass-forming region of SiO_4 -PbO was in the region of 60-70% PbO, which suggests that Pb must participate as a network former (Goldammer et al., 1994).

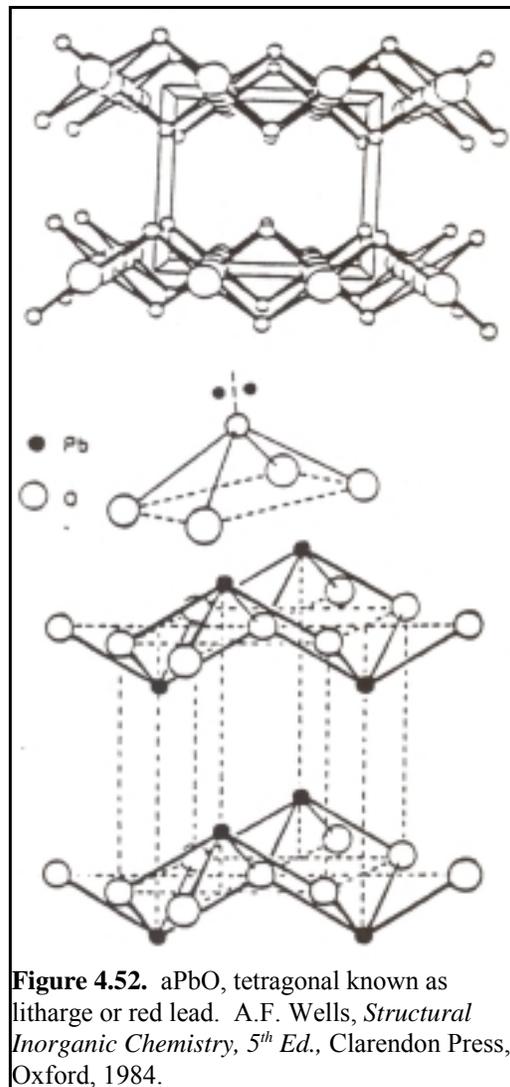
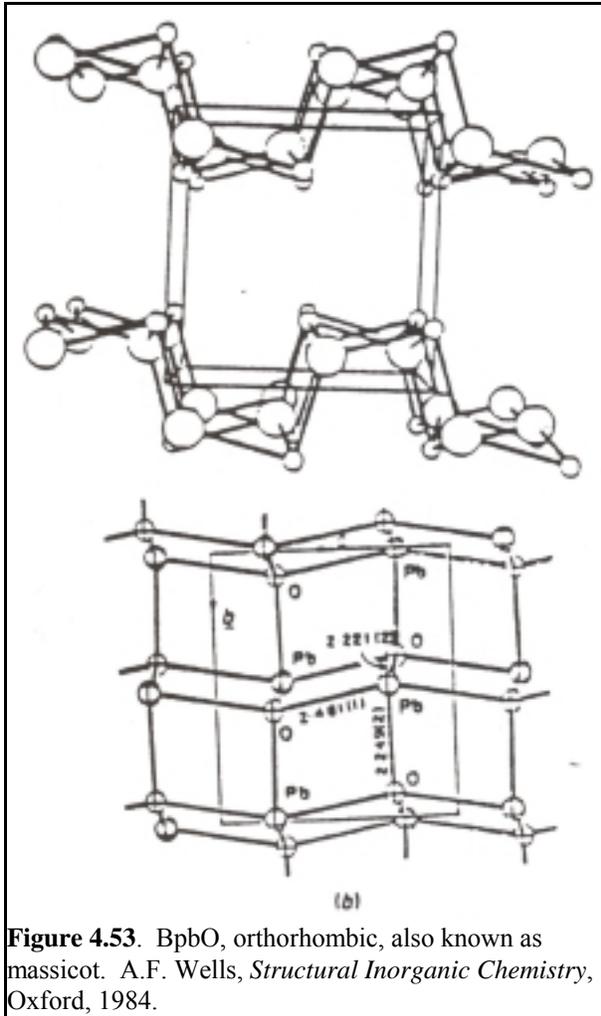


Figure 4.52. α PbO, tetragonal known as litharge or red lead. A.F. Wells, *Structural Inorganic Chemistry*, 5th Ed., Clarendon Press, Oxford, 1984.

We can approximate the structure of leaded glass if we start with a model for the structure of the mineral pyromorphite (Figure 4.56 for the structure, and Figure 4.57 for the mineral) (Stemmermann et al., 1991). A similar model can be proposed for lead silicate glass. The PbO side chains help stabilize breaks in the SiO_4 tetrahedral chain and thus keep the directionality of bonding while breaking the three-dimensional network. The proposed model assumes a structure of $[\text{Pb}_{40}(\text{Si}_2\text{O}_7)_6(\text{Si}_4\text{O}_{13})_3]\text{O}_7$. Others have concurred with the hypothesis of PbO_4 pyramids intercalated within Si di-tetrahedra ($\text{Si}_2\text{O}_7^{6-}$) (Morgan et al., 1991). Still others think that the open structure of the chains results from the lone pair of s electrons on the divalent lead (Khalifa et al., 1987).



Lead and Ease of Handling

A further consideration for use of a metal in glassworking is its ease of handling. It needs to be capable of good thermal expansion. In other words, it must not crack on cooling. Thermal expansion of glasses comes from atomic vibrations in the lattice. Repulsive forces increase more rapidly than attractive ones as atoms move together. Thus it is more difficult to bring atoms together on heating. Consequently, it is expected that heating and bringing atoms into motion will cause more expansion than contraction. The tetrahedral bond must be able to accommodate the change in angle brought about by expansion. This change can be affected in an oxide as opposed to a pure carbon system (e.g., diamonds). Thermal expansion has been related to the electrostatic share

(valency/coordination number). The smaller the electrostatic share the easier the expansion. A comparison of SiO_4 to tetrahedral lead, PbO , found that the electrostatic share of the silicate is $(4/4 = 1)$ while that of lead is smaller $(2/4 = 0.5)$. Thus lead should increase the thermal expansion of the silicate melt.

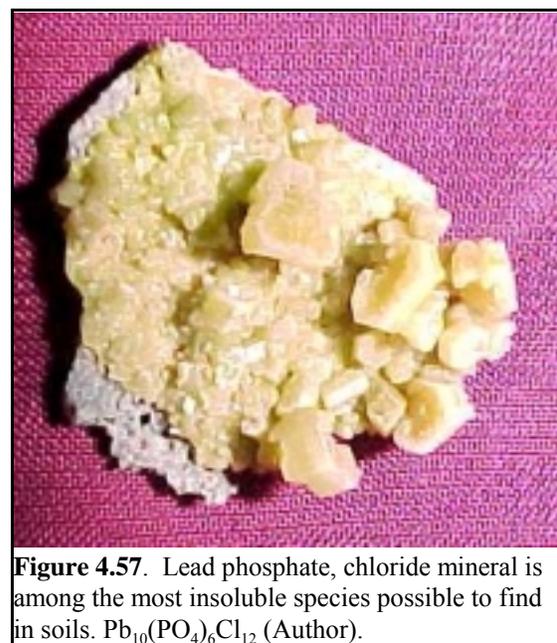
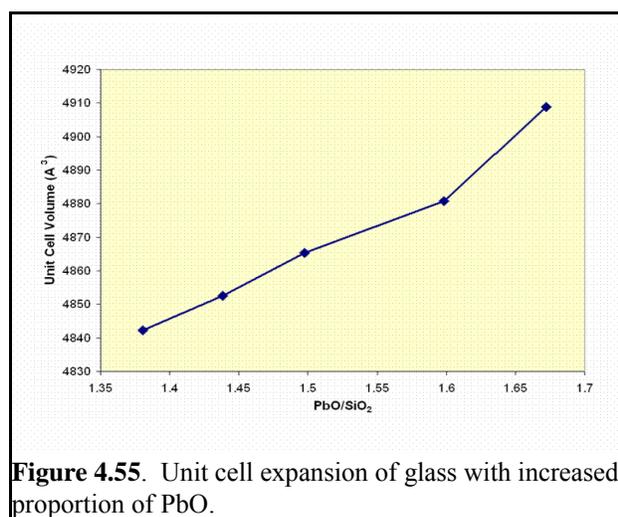
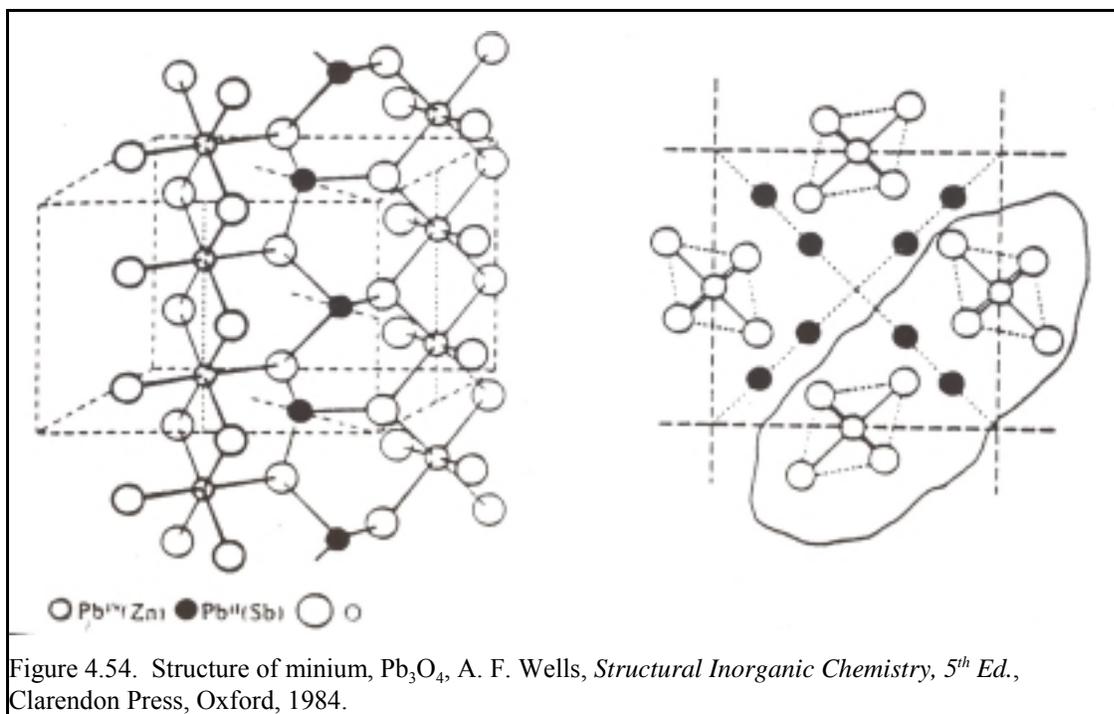
The spreadability of a glass, which is related to its viscosity, plays an important role in the manufacturing process. The ratio of force to displacement (flow), is called poise. Poise is a measure of viscosity. In glasses, viscosity changes rapidly as a function of temperature, so rapidly that it is plotted on a logarithmic scale. This rapid change in viscosity accounts for the ability to “blow” glass. Figure 4.58 shows the viscosity-temperature relationship. G is pure silica, A is silica with Cu, Mg, Na and K additions while B contains 29 weight % PbO #####.

Addition of lead, with its weak tetrahedral bond-forming capabilities, lowers the viscosity of the glass at any given temperature, or conversely, the temperature at which a given operation is performed can be lowered (Table F.12) Unleaded glass requires a temperature of 1500°C to soften; leaded glass, 580°C . The latter temperature can be attained by a campfire. The dramatic effect of lead may be due to the inter-chain distance associated with the presence of lead oxides. The large distance between spaghetti strings is created by the lone pair of electrons on lead. This lone pair, because it requires a greater chain spacing, causes the material to be more malleable – in other words, less viscous (see Figure 4.2).

Lead and Opacifiers: Production of Opacifiers

White opaque glass contains lead and tin. An opacifier is a substance that does not impart color and that has a large particle size ($0.35 \mu\text{m}$ to $1 \mu\text{m}$ (Rooksby, 1939). Its size makes for a large light-scattering center. SnO_2 (cassiterite) has Sn^{2+} with an electron configuration of s^0d^0 . There are no electrons to interact with light. Thus this compound is “invisible” to light in color-forming range. SnO_2 crystals reflect light back without absorbing any particular wavelength and consequently appear white. (See Chapter 5 for more on color.)

The structure of cassiterite is tetrahedral. It has a density of 6.95 g/cm^3 . Cassiterite is obtained through the oxidation of tin metal. While tin can be oxidized at reasonable temperatures, it becomes coated with a dense layer of oxygen. This layer, unlike lead



does not conduct oxygen well, thus further oxidation is prevented. Adding a small amount of lead (at a ratio of 1:1) facilitates the oxidation of ground tin (Freestone et al., 1988). This difficulty may explain why lead/tin opacifiers appear rather late in history. In 1959 Rooksby asserted that SnO_2 does not show up as an opacifier until the Venetian glass of the late 1400s (Turner and Rooksby, 1959). He later indicates that

SnO_2 was in mosaic with 20-30 μm sized particles from Roman Spain (Turner and Rooksby, 1962).

An early white opacifier was based on antimony. $CaSb_2O_6$ was a typical opacifier in ancient Egypt. The beautiful Portland vase (Figure 4.10) seen

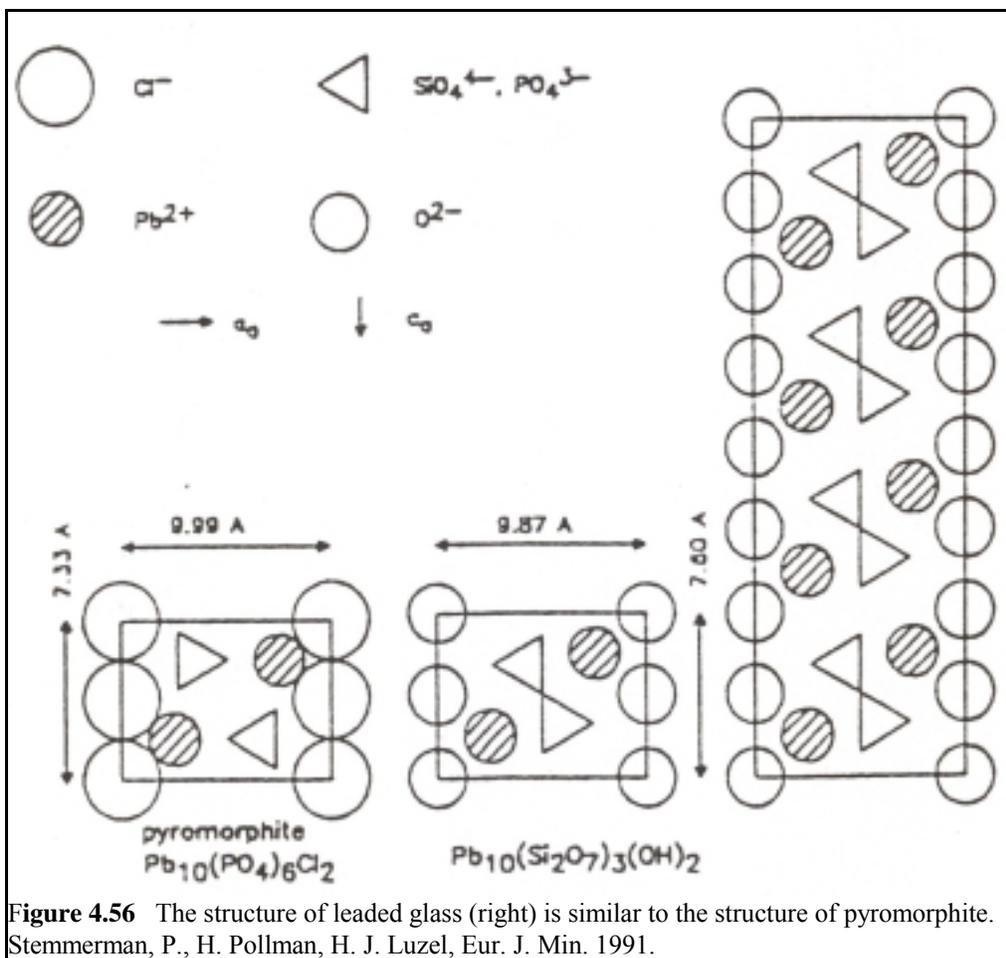


Figure 4.56 The structure of leaded glass (right) is similar to the structure of pyromorphite. Stemmerman, P., H. Pollman, H. J. Luzel, Eur. J. Min. 1991.

earlier contains the calcium antimonate. Antimony is fairly inert with respect to light. Like tin and lead, it is a post-transition metal, meaning that it has filled d orbitals that cannot interact with light through d orbital splitting. The combination of lead and antimony apparently occurred because of the simultaneous addition of lead for low temperature work and addition of antimony to create an opaque glass. Other opacifying agents are $\text{Pb}_2(\text{AsO}_4)_2$ and $\text{Pb}_3(\text{PO}_4)_2$.

When the lead composition is increased in either tin or antimonate glasses, lead can crystallize either as a lead/tin or a lead/antimony compound. When the lead to tin ratio is 8:1, PbSnO_3 forms, resulting in an overall yellow compound (see Chapter 5). Similarly, lead forms a PbSb compound that imparts a yellow color to the glass.

Lead and Brilliance

One of the desirable properties of glass is its

shine. How might lead make glass shiny? The shine of the glass surface is a function of its ability to reflect light. Reflection of light proceeds by a transitory (virtual) absorption of light and its re-radiation. In other words, light interacts with the polarizable electron cloud in the matrix. The ability of a surface to reflect light depends on its total number of easily deformed electron clouds. A simple plot of the atom's density should be a good measure of its total electrons and thus of the material's refractive index. Here refractive index can be described as follow (Atkins, 1978, p. 756):

$$[4.2] \quad \alpha_v = (3M/L\rho) (n_r^2 - 1)/(n_r^2 + 2)$$

where α_v is the polarizability of the material at a given frequency of electromagnetic radiation, M is the molar mass, ρ is the density, L is Avogadro's number, and n_r is the refractive index of the material. The higher the number of electrons and the more weakly they are held,

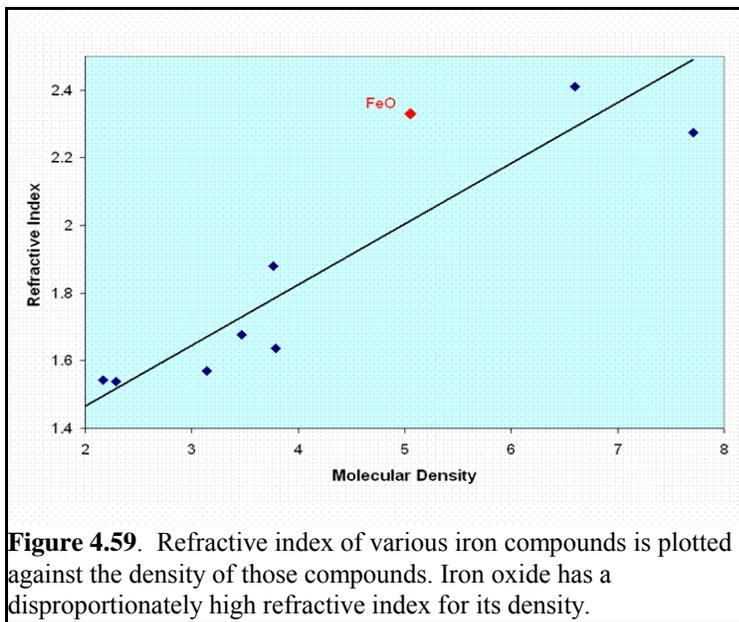


Figure 4.59. Refractive index of various iron compounds is plotted against the density of those compounds. Iron oxide has a disproportionately high refractive index for its density.

the more polarizable they are and the longer the material retains the electromagnetic wave. Because lead lies low in the periodic table and has a large number of shielded (weakly retained) electrons, it is highly polarizable. It thus should have a higher refractive index than other metals (Table F.17).

A high refractive index means that at a metal/air interface, light is highly reflected, resulting in a shinier surface:

$$[4.3] \quad I_R/I_o = (n_2 - n_1)^2 / (n_2 + n_1)^2$$

where I_R/I_o is the ratio of light reflected to original light and n is the refractive index of the material. The information in Table F.17 about pure metals seems to support this hypothesis, but what happens when the metal is combined with oxygen, as it is in glass?

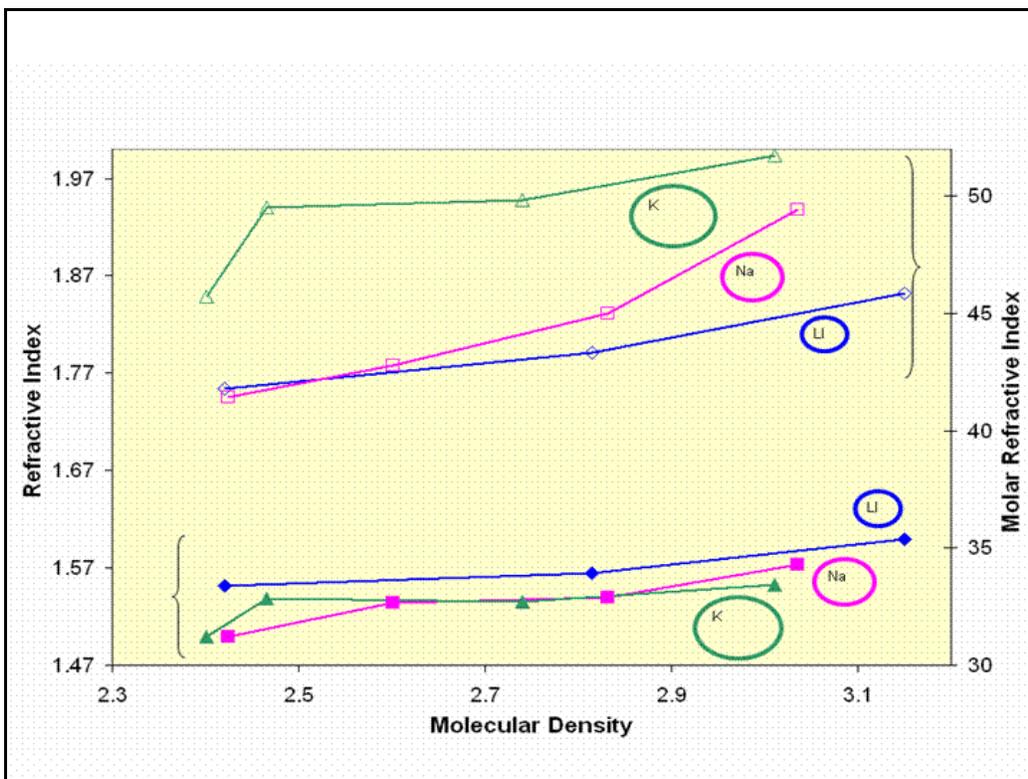


Figure 4.60. Molecular density of glasses modified with K, Na, and Li alters the refractive the molar refractive index in a predictale fashion as compared to the refractive index. Data source: A. Paul..

Figure 4.59 shows the refractive index of many iron compounds such as chlorides and nitrates. Note that FeO deviates from the prediction we might make based on compound density. This deviation suggests that the oxygen content within the glass plays a role in the control of the refractive index (Figure 4.60). In order to account for this effect, the term for the refractive index must be modified. It must account for the

number of moles of oxygen within a given volume. This modified term is the molar refractive index first introduced by Berethelo (1856):

$$[4.4] \quad R_m = \frac{M(n^2-1)}{(n^2+2)d}$$

where M is the molecular weight, d is the density and n is the refractive index. The important feature of this equation is the decrease in the molar refractive index as the density of the material increase. How does metal oxide density affect the ability of electrons to move? If the cation volume is held constant, then lowering the density, that is, increasing the volume occupied by the oxygen, will increase the polarizability of the oxide because the electrons are now occupying a larger volume around the oxygen. These trends can be seen in Table F.15 and F.16.

Note in Tables F.15 and F.16 that the fact that the normal refractive index does not appear to follow any trends with modifier, particularly with the density. However, the molar refractive index increases with movement down the periodic table. This increase indicates that the molar refractive index is a measure of the cationic charge density. As the cationic charge density increases (Ba<Sr<Ca<Mg) there is more attraction of the oxygen electrons (more sharing) and less polarizability. The result is a lower molar refractive index.

The periodic trends in molar refractive index also give rise to theme of “basicity” of the glass melt. The negative fragment of the severed glass chain is normally stabilized by added cation. The cation and anion can ionize, just as an acid and base:



The larger the cation R, the less the cation’s charge density and attraction to oxygen electrons, and the greater the ionization and basicity of the glass. The basicity follows this sequence: CaO<SrO<Li₂O<BaO<Na₂O<K₂O. This sequence is predictable from trends in the periodic table.

This basicity trend suggests why lead makes glass more brilliant. Lead is quite low in charge density because of its d¹⁰s² configuration, the same

reason it melts so easily as a metal. Consequently, lead does not easily pull electrons from oxygen. Those oxygen electrons become more accessible for interaction with light. Tables F.15 and F.16 shows the high molar refractive index values of several oxides.

Lead as a Glass Solvent Enhancer

Glass solvation of metal ions can be used to induce various colors. Transition elements contain d

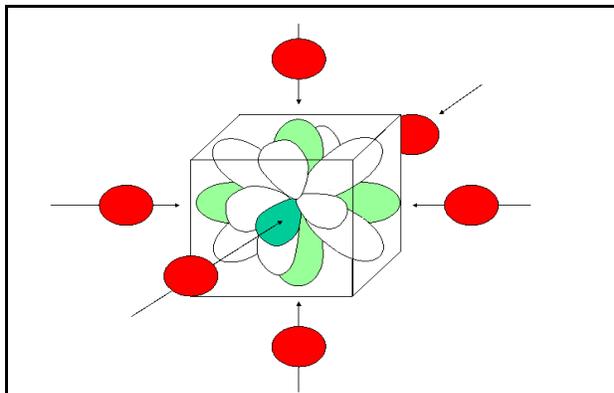


Figure 4.61. D orbitals lying along the x, y, and z axis are perturbed by incoming ligands (solid circle).

rw electrons which occupy orbitals of the shape shown in Figure 4.61. When the metal cation is approached by a charge-compensating anion, the orientation of the approach is governed by the charge density of the overall cation and by packing considerations. When the coordination number is six, the most efficient packing occurs with an octahedral arrangement that allows four of the six approaching anions to come into close proximity with the metal's existing d orbitals. The charge repulsion of the d electron for the incoming anionic charge makes these orbitals higher in energy. Thus, depending on their number in the transition metal, the d orbital electrons will preferentially occupy off-axis (lower energy) orbitals. These low-lying d electrons can, with the right amount of energy from light, be excited into a $d \rightarrow d^*$ transition. This transition creates a loss of light intensity at that wavelength, which is perceived by the human eye as color (see next chapter.)

The primary coordinating anion in the glass comes from the oxygen ionized in the acid/base reaction just described. As we have seen, variable amounts of the additive within the melt can change the direction of the ionization equilibrium and produce differing amounts of O ligands. When few potential O ligands are present, the coordination number of a transition metal within the melt may change from 6 fold

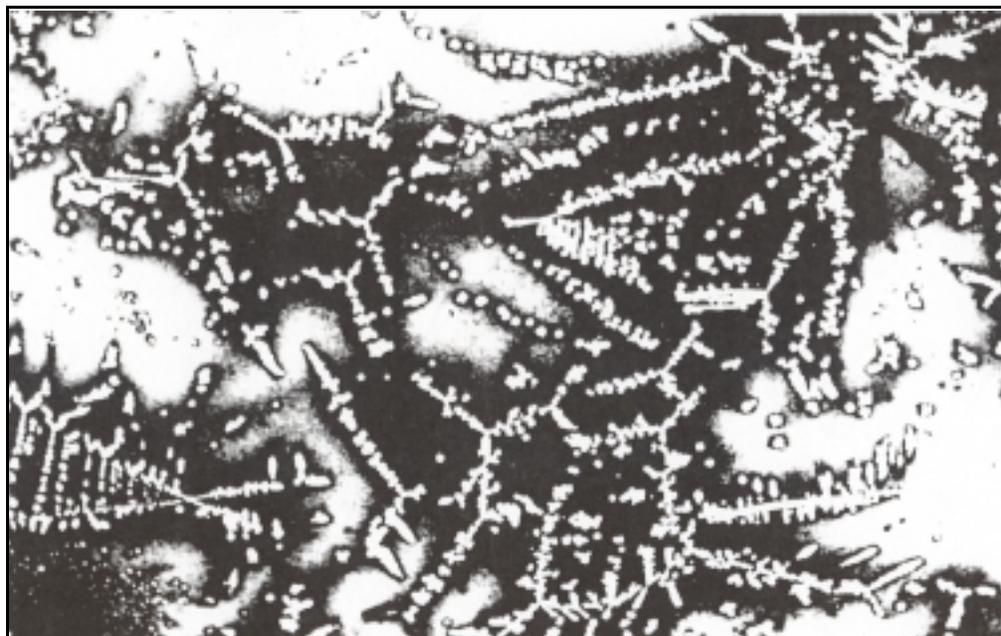


Figure 4.62. Cu_2O dendrite formation in ruby red glass gives rise to the color observed. Lead allows copper to move through the molten glass to reach the growing dendrites. (Image from I. C. Freestone).

(octahedral) to 4 fold (often square planar). This change destabilizes the d orbital into a different energy pattern and thus a different wavelength of light is absorbed. Consider the example of cobalt. Cobalt glass changes from blue (coordination number (C.N.) 4) to pink (C.N. 6). These principles can also be observed in the color changes of nickel in a glass melt as different substances are added. Recall that as the glass modifier moves down the periodic table, the ionization of the silica chain increases, increasing the number of ligands, and increasing the ligand strength. Li_2O added to nickel glass promotes a yellow color, while addition of Rb_2O leads to a coordination number of 4 for nickel and a violet color.

A second source of color in glass arises from the presence of small crystals of metal oxides (as opposed to d, orbital splitting). In these metal oxides, there can be a charge transfer process, that is, an electron transfer between the metal and the ligand. The energy of this process can coincide with visible light to give color. Cu_2O gives a charge transfer process that results in a perceived red color.

Copper becomes soluble owing to the glass melt basicity when PbO is present. The ionized lead oxide chains can stabilize the metal cations and their oxides. This property makes lead a good reagent for metal purification processes and the production of SnO_2 . This same property makes leaded glass an excellent solvent of metal ions. Lead is added to glasses to increase cuprous oxide solubility and thus increase the amount of red color (Brill et al., 1974).

The leaded glass increases the concentration of copper within the melt, allowing the growth of larger Cu_2O crystals. In highly leaded glass melts, cuprite (Cu_2O) can crystallize in a dendritic structure (Figure 4.62). Cuprite's color depends upon the size and shape of the dendrite. Large-textured dendrites give rise to red, while fragmented dendritic structures result in a brownish color (Freestone, 1987?).

As noted in the previous discussion of dendritic growth in bronzes, the type of crystal grown depends upon solidification from a multiple phase material as cooling proceeds outside inward (for metal casting). As the temperature drops, various components of the material begin to nucleate, and leave behind a melt higher in the remaining melt components and lower in incipient solid material. Lead oxide, for instance, remains molten and thus allows transport of copper down a concentration gradient via oxygen linkages to the growing crystal. As a result, the lead oxide promotes dendritic growth in glass even though it prevents such growth in bronzes.

An alternative explanation is that additives of lead to the glass replace Na and Ca preventing the possibility of forming diopside ($\text{CaMgSi}_2\text{O}_6$), a compound which can prevent the formation of the glass phase.

Red glasses were among the first produced. They were made with a significant amount of lead oxide. Some of the earliest ruby glasses from Nimrud contain 22.8% PbO (Turner, 1959). We saw that red glass was used throughout Roman times and traded to the Celts. The 12th century author Heraclius (*De Coloribus et artibus Romanorum*) writes:

Accipe plumbum optimum et nitidum, et pone in ollam novam, et arde in ignem, usque quod pulvis sit (Take the best shining lead and place it in a new pot, and burn it in the fire until it becomes a powder).

This powder is to be mixed with sand 3:1, then melted in a crucible with copper for coloring (Charleston, 1960). Into the late medieval period, ruby glasses were made with lead oxide as a solvent. Glass specimens from 1400 A.D. contain 2-3% PbO (Brill, 1968).

Modern Glasses

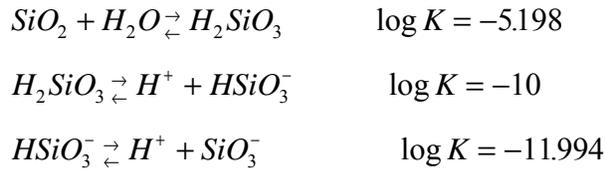
Today lead is used in radiative absorption glasses, as well as glasses that have unusual conducting properties, such as lead fluorosilicates. In these F^- moves at a faster rate than other anions because the Pb-F bond is relatively weaker than the strong F-Si-O bonds of pure fluorosilicate glasses. Because the Pb-F is weak, it can be disrupted, leaving F^- mobile (Morgan et al., 1991). As F^- moves, charge imbalance within the glass can result in a measurable voltage. This voltage can be calibrated to the amount of F^- in the glass, making it a chemical sensor.

Lead titanate glass is a perovskite type crystal. Similar structures are superconductors. Lead titanate is used for ferroelectric piezoelectronics (Lee et al., 1996).

Glasses containing heavy metal oxide centers can be used for scintillation detectors and medical images. The large polarizability of the heavy metal oxides give rise to optical non-linear devices in which a photon absorbed is re-emitted at a different wavelength (George et al., 1999).

Chemistry of Lead Glass and Glaze Toxicity

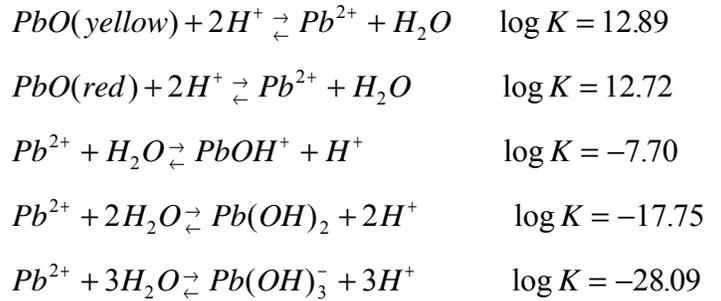
The potential toxicity of leaded glasses arises from the acid base reactions of the two main components in the leaded glass: silicate and lead oxide chains. Vitreous silica, glass, is hydrated at the surface to form an acid H_2SiO_3 . This acid has the following equilibrium reactions with the solution:



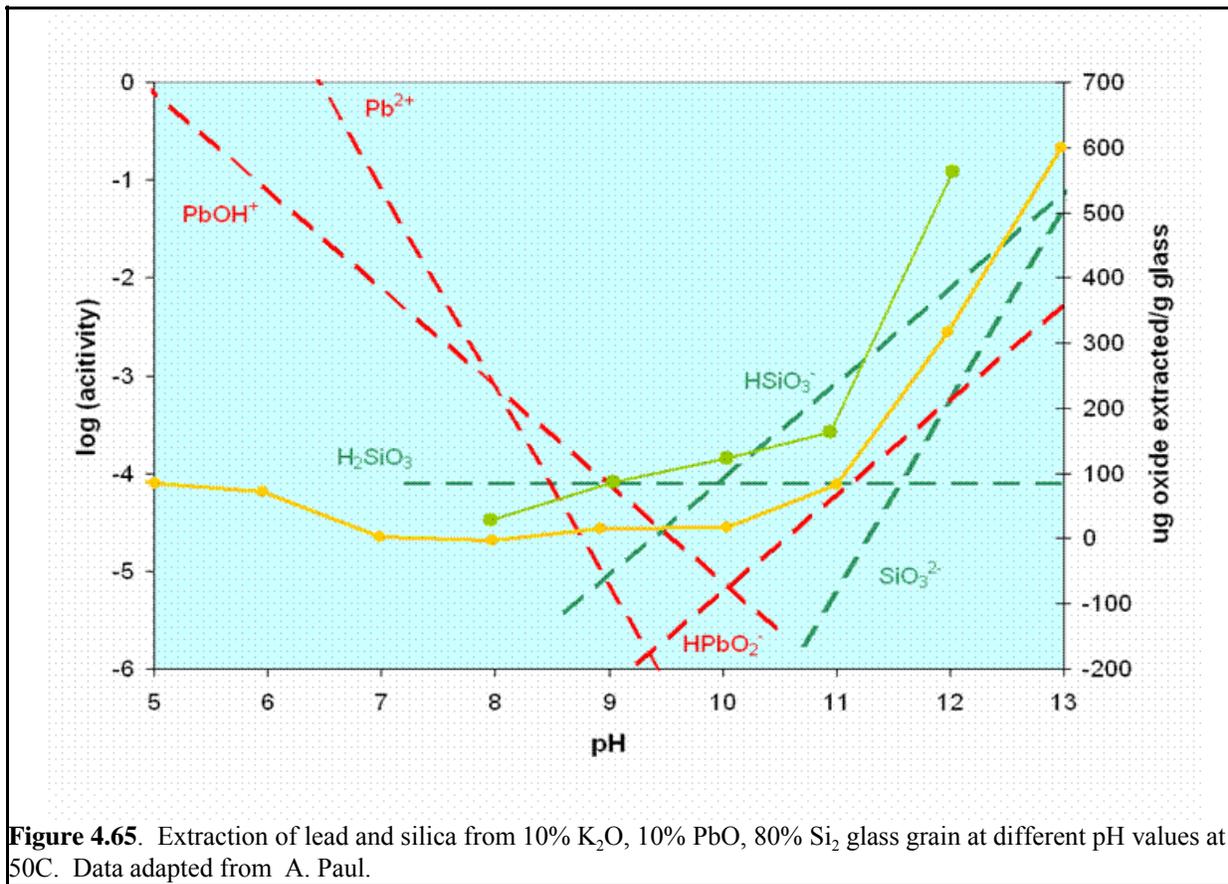
As protons are removed soluble anionic species are formed. We expect that glass which is exposed to high pH solution will dissolve (Figure 4.63).

Lead oxide chains are also soluble based on the pH of the solution (Figure 4.64). At low pH the lead oxide is protonated and or the oxide removed. At high pH an oxygen is added:

The stability of glass and lead oxide is shown in Figure 4.65. This figure indicates that leaded glass will



dissolve at either very low or very high pH. Dissolution of the glass will result in liberation of lead into the solution.



B. Chemistry of Lead in the Majolica Glaze

Lead effect on Surface Tension

In leaded glaze, lead serves much the same purpose it does in glass. It lowers the temperature of the melt and serves as a solvent for the metal oxides used in pigmentation. The low temperature melt allows pottery to be well-sealed, i.e., to have low porosity, without the elevated temperatures (around 1400 °C) required for porcelain (Figure 4.22). Typical manufacture involves the formation of the pot, drying it in fire to shrink it somewhat, painting it with the glaze, and using a second low fire temperature to melt the glaze over the surface. Painting over the surface of this low-fire lead glaze results in the slightly wavy look of the Talavera ware, or in the running glaze of the sancai ware.

Evidently, in glaze production, it is important to know how to control the run of the melt on the three-dimensional body. Alumina is added to the glass to increase the viscosity (Rhodes, 1974, p. 79). The viscosity must be raised to lower the run, but the glaze must be made stickier if it is to stay in place.

A glaze's spreadability is related to the surface tension of the melt. The surface tension depends upon the energy of interaction in three places: between the molten glaze and the air interface, between the solid body and the air interface, and in the area of the solid/liquid contact (Parmalee, 1973, p. 193). The surface tension is most easily measured as the contact angle of a drop with the surface. When the drop beads up there is a high surface tension. Figure 4.66 shows the surface tension due to the composition of a glaze in weight percent. The larger the amount of SiO₂, the greater the surface tension and the less the wettability. Various oxide additives change the surface tension at 900 °C. Lead oxide reduces the surface tension on the clay body the most, for the same reasons that it serves as a good solvent. It thereby increases the wettability of the glaze.

In addition to creating a solvent for color, reducing firing temperatures, and having good wettability, the lead glaze does not strain or crack on cooling. If strains or cracking are to be avoided, the volume change of the clay body must be matched with the volume change of the glaze while maintaining fluidity (for adhesion) and rigidity (to avoid running of the glaze). The type of clay used both as part of the glaze and in the body affects the volume change. α quartz has a large volume change at close to 600 °C, while β quartz has a large volume change at 200 °C

(Parmalee, 1973).

Modern Leaded Glazes

Non-ceramic glazes, or thin lead-based film glasses (coatings) are still made today. They are used to make anti-reflective films, solar panels, heat sensitive windows, and optoelectronic materials.

SUMMARY

Lead played an essential role in the development of glass technology because it lowers the temperature at which glass can be manipulated. This beneficial effect is caused by the fact that lead forms tetrahedral chains of oxides with a lone pair set of electrons that creates some distance between chains and thus an internal grease. Lead combined with antimony at low levels creates a white opacifier. Lead combined with antimony at high levels forms a brilliant yellow color that was much admired by early glassworkers. Lead serves as an excellent solvent for various d electron color-forming metals because it changes the basicity of the glass melt. This solvent effect is identical to the one that allows lead oxides to "purify" silver of other metal oxides. Lead also changes the basicity of a silicate melt and promotes transport of copper through the melt so that it can form oxide dendrites that give a red color.

Lead is important in glazes. The low temperature and good covering power of lead glaze allowed low porosity vessels to be formed with much less energy cost than that involved in forming porcelain. Glass technology has developed without interruption from early Mesopotamia to the Roman Empire to northern Europe to the modern era. Glaze technology arose primarily from the substitution of pottery for bronze burial objects in China. The Chinese technology was carried west across the Silk Road, where it influenced the emerging Islamic states. There a tin opacifier glaze was invented which required the presence of lead to facilitate the production of tin oxide. The Islamic culture carried lead glazing in the form of majolica to Spain. From there, by the Renaissance it made its way to northern Europe and then to England. It went directly from Spain to Mexico and the was distributed through other Spanish colonies.

Chapter 4: Problems

Glasses

1. Where did glass technology arise? Under which empire?
2. How did the Egyptians acquire glass technology?
3. How did the Romans acquire glass technology?
4. How did glassmaking arrive in Northern Europe?
5. When was “leaded” or rock crystal glass “invented”?
6. Describe how a core-formed glass is made.
7. What are the five main reasons for adding lead to a glass?
8. Was there a link between Celtic use of red glass and its production in the Roman Empire? If so, how was this link determined?
9. Why was the coal furnace a “necessary” invention?
10. What side benefits did the coal furnace bring to glass production?
11. Which product drove the huge increase in the glass industry after the invention of the coal furnace?
12. In early China, what was the relationship between the use of copper/bronze objects as burial objects and the high degree of technical expertise concerning pottery?
13. What is sancai ware? What objects were typical for sancai ware? To what time period did they belong?
14. When did the Chinese navigate the Silk Road?
15. What impact did the development of white porcelains have on leaded glazes in the Middle East?
16. What is Iznik ware?
17. Why was a lead/tin glaze so rapidly adopted throughout Europe?
18. What role did the diminishing power of the guilds have on pottery development in Europe?
19. Who brought leaded glazes to France?
20. Who brought leaded glazes to Germany?
21. Who brought leaded glazes to Mexico?
22. Who brought yellow ware to the United States?
23. Where were the Mexican leaded glazes distributed?

24. Why is leaded glaze production still very prevalent in Mexico?
25. What makes lead glazes so toxic?
26. Why does the production of citric acids in lead glaze wares enhance lead removal?

More Chemically Related Questions

27. What elements are primary glass formers? Where do they lie in the periodic table?
28. What is the role of a modifier in glass formation?
29. Why is lead so effective at modifying glasses?
30. What happens to the unit cell when lead is added? How does this change affect the ease of handling?
31. What property of lead in a glass makes it especially useful for counterfeiting gemstones?
32. Does the property listed in (31) belong to lead by itself, or to lead oxides?
33. Why is lead a good “solvent” for other metals in glass?
34. Why is lead associated with red glasses?
35. What percent lead is typical for a red glass?
36. True or False: low pH solubilizes silicon over lead.
37. In addition to the five reasons listed above for use of lead in glass, name one reason to use lead in glazes?
38. How does evaporation during the glazing procedure stabilize lead?

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