A physicochemical study of Medieval and Post-Medieval ceramics from the Aegean

Panagopoulou, A.

Citation

Panagopoulou, A. (2023, May 9). *A physicochemical study of Medieval and Post-Medieval ceramics from the Aegean*. Retrieved from https://hdl.handle.net/1887/3620224

CHAPTER 6 GLAZES, PIGMENTS AND CLAY VITRIFICATION IN GENERAL

6. INTRODUCTION

In this chapter, I try to investigate from the chemical as well as the archaeological point of view variant ways to approach colour and glazes and to combine them with a scientific approach in the next chapters. I tried to explore and express the potters' visions, aesthetic perception and even intuition and subsequently I tried to determine the pigments and all the hues that were created by them by physicochemical analysis.

Ceramics has played a role in colour development . The ceramist or potter approaches colour firstly from a technical aspect: the colours of the clay, slip, oxides, etc, and what effects can be achieved with different glazes alone or in combination. The development of a broad range of glaze, underglaze and on-glaze decoration has produced a larger palette of colours. My need for greater understanding of colour theory and mixing, the application of colour and the development of pattern in relation to form, it was now required as the colour can be examined from a variety of perspectives. For this reason, in this chapter, I describe the chemistry but also the chemical reaction of the glazes, the decoration techniques of pottery, firing, fluxes and clay.

6.1 HISTORY OF THE GLAZE TECHNOLOGY

The earliest glazes appeared in ancient Egypt and were applied to faience objects. Faience was ceramic which contained high percentages of silica, holding these alkaline glazes well. Unless a colourant 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 them from being dissolved, they were burned together with silica to create a solid mas, which was then ground and crushed to create a frit and then applied to the object (Tite et al. 1998; 2007). The main difficulty which emerged from the use of this alkaline/silicate glaze was its inability to adapt to the expansion and contraction of pottery. Hence, alkaline glazes did not adhere well to pottery. An estimated 99% of ancient clay ceramics were unglazed. The transition to glazed pottery was facilitated only by lead glazes which had the advantage of following pots' thermal expansion and contraction, so that the glaze did not crack upon cooling. Despite the early date of this recipe, lead glaze was not widely used in the Middle Eastern/Mediterranean world until the first century BC (Hatcher et al. 1994). The consistency of the glaze recipe throughout the Roman Empire suggests a standard procedure used all over the Empire (Fitch 2003).

Ashurbanipal's Nineveh library preserved a Babylonian glaze recipe from 800 BC:
24.3 parts glass
40 parts lead
50 parts copper
5 parts tin
3.1 parts saltpeter

During the T'ang dynasty (618-906 AD), the exceptional skill of the Chinese potters culminated in the development of porcelain. 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 ^{o}C) in order to be fused. Firing results in a glass-like translucent ceramic. The fused product has a high refractive index and many scattering centers. The low porosity creates a glass-like hardness in the porcelain. Porcelain production in China reached its peak during the Song (960-1280 AD) and Yuan (Mongol) (1279-1368) dynasties. However, export of porcelains had already begun around 900 AD with Muslims in the port town of Quanshour, Fujian Province, controlling the trade of porcelain throughout the Islamic world. White porcelain with blue cobalt glaze was exported via the Silk Roads having a great impact on the history of lead. Islamic potters could not reproduce porcelain because they were not working with kaolin clays fired at high temperature. They did, however, invent a white high-luster ceramic called *Maiolica* through a process of lead-tin glazing. Then the Ottoman ceramic tiles based on tin glazes (Karmason and Stacke 1989), particularly of the Iznik ware variety from northwest Anatolia were produced in large numbers.

Abu'l Qasim Kasani 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 and gives a white colour. This base is then overcoated with a lead glaze to give additional brilliance. The presence of the lead produces a brilliance that simulates the translucence of porcelain. The presence of tin oxide produces the white background. In addition, this tin/lead glaze allows for lower temperatures in the pottery-making process. Although pots fired at lower temperatures are more porous, the lead glaze achieves a sealing glassy state at such temperatures (Figure 82) (Fitch 2003). The technology of lead glazing with tin was transferred from the rest of the Islamic world to Islamic Spain where production was centered near Valencia. The technology was initially used in southern Spain, particularly in Talavera de la Reina (Figure 83). The export of this glaze coexisted with the weakening of the strict guild system in Europe. This period pottery artists joined with painters to develop a style of painted figure-based pottery called *Maiolica* 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 appeared 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. Cipaino Michele di Piccolpasso described the classical Italian Maiolica in 1524-1579 AD 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. Bernard Palissy who worked from 1550-1570 dominated French leaded glaze ware. After a trip to Italy, Palissy spent many years and his entire income trying to develop a lead/tin glaze. Palissy helped to bring about the transformation of science from an alchemical art to modern style of inquiry and he accomplished it. He studied the recipes of the monks who wrote the *Mappae Clavicula*, 900 AD (Smith and Hawthorne 1974; Fitch 2003):

Recipe 281: A White Glaze
The white pigment: 10 pounds of tin and one pound of lead reduced to powder [by calcination] 10 lbs of Asian alum, 8.5 lb of yellow sand. Make a furnace and fire it, and after the cooking break up the cooked stuff and sieve it. Next add to it 9.5 lbs of similarly sifted sand, and then 6.5 lbs of lead and 5 lbs of tin [calcined] in the same way as described.

Recipe 283: The blue-green pigment
10 oz of cleavable alum and 5 oz of sand and 4 oz of white rounded stones, all of them roasted and sifted and 4 oz of lead and 1/2 ox of [?] and 15 [?] Of silvery [?].

6.2 GLASSES AND GLAZES

Glasses represent a phase of matter between solid and liquid. Glasses are essentially supercooled liquids. 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 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. 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, which are conducive to three-dimensional network formation (Zarzycki 1991). Among the tetrahedral network formers is SiO_2, the basis of quartz.

The difference in bonding between a crystalline solid as quartz and glass is that the network in quartz is three dimensional and rigidly linked; the glass network is more distorted. In glass, the polyhedral 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 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. In a series of tetrahedral connected only at the corners, the apical oxygen atoms with lone electron pairs can be stabilized by other modifying polyhedral chains or cations (Figure 84) (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 (crystalize) starting at nucleation sites (Muller et al. 1993). The 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. The species that easily form glasses are close in size and electronegativity to oxygen, they have relatively high bond energies (Fitch 2003).

A glaze is simply a continuous layer of glass coating the surface of a ceramic. Glazes have compositions similar to those of other glasses except that more alumina is added to render them less fluid at high temperatures so that they do not flow down the vessel wall. The glaze provides a hard, nonabsorbent, impermeable, easily cleaned surface and allows for a variety of colours and surface textures. It also adds strength by painting, pouring, dipping, or spraying a water suspension of the ingredients. The glaze may be applied to and fired on a raw body or applied to a once fired body in a second glost firing. Glazes may be clear, coloured, or opaque; contain tiny or visible crystals; and have glossy or velvety matte surfaces. We refer to a coloured decorative glaze layer applied on top of a base glaze as an overglaze enamel. Potters concerned with glazes usually divide compositions into ‘raw’ glazes, which contain naturally insoluble raw materials, and ‘fritted; glazes, in which soluble (or poisonous) ingredients are reacted or melted to be made insoluble before mixing with other ingredients. A glass usually has/contains 60-70% silica (but perhaps as little as 30% for a high-lead glaze or one in which boron oxide replaces some of the silica). There should be a few percent of alumina for adequate viscosity, and the rest should consist of alkalis and alkaline earth materials that act as ‘fluxes’ to lower the melting point. According to their purposes, the constituents were divided: alkalis and alkaline earth elements as modifiers or fluxes (K_2O, Na_2O, CaO, MgO, PbO – in general, R_2O and RO where ‘R’ is any metal); intermediates (R_2O_3 such as Al_2O_3, Fe_2O_3); and glass formers (SiO_2, B_2O_3, RO_2) (Weyl 1951; Rhodes 1959; Singer 1963; Rye 1981; Kingery 1986; Rice 1987; Constant and Ogden 2000; Fitch 2003).

Depending on their **composition**, ceramic glazes are distinguished in:

- **Lead glazes.**
  They are formed from acidic silicate lead salts. They have high brightness; they are very fusible and durable. They are usually used for low-temperature red clay glazes.
- **Alkaline glazes.**
  Apart from silicon and alkaline oxides, they contain a high percentage of aluminum oxide. They are characterized by high hardness and transparency. They are used usually in porcelain. At low temperatures they are used as bases in raccoon glazes, luster and crack decorative techniques.
- **Boron glazes.**
  They consist of boron oxide and silicate salts combined with alkali, alkaline earth and lead oxides. They are applied to some faience (Weyl 1951; Rhodes 1959).

Depending on the **melting point** of the glazing or depending on the materials of which they are made, the glazing is divided into two categories:

- **Low Temperature glazes.**
  Indicatively, they contain two parts of silicate (silicon) per one part of the other components. Firing temperature is often in the range of 1.000 ^{o}C (or slightly lower in some cases).

- **High Temperature glazes.**
  Indicatively, they contain three parts of silicate (silicon) per one part of the other components. Firing temperature is often in the range of 1.200 ^oC (or higher in some cases). These glazes are characterized by greater durability (temperature, corrosion, etc.) and increased hardness.

Depending on their basic melting component, glazes are often distinguished into lead, boron, feldspar, etc. (Rye, 1981). The glazes depend on the effect of oxides on the eutection and viscosity (Table 10) (Matthes 1985).

Desirable Properties of Leaded Glass or Glaze

Lead and glass-making are even more intertwined throughout history than lead and metallurgy. The reason is that lead gives glass or glazes several desirable properties.

1. Lead renders glass or glaze less viscous and is thus easier to work with at lower temperature. This reduces also energy costs.
2. Lead lowers the heat of expansion of the glass or glaze 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 producing coloured 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 red colour (Fitch 2003).

6.2.1 RAW GLAZES

Among the most common glazes made from naturally insoluble ingredients are porcelain and stoneware glazes that contain limestone and feldspar as the principal source of fluxes. Pegmatites, China stone, and similar mineral mixtures of quartz, clay, mica, and feldspar can be used as natural glazes. The other principal raw glaze category covers the lead glazes, in which a principal constituent is red lead (Pb_3O_4), litharge (PbO), or white lead ($2PbCO_3 \cdot Pb(OH)_2$). Litharge is the oxidation product formed on molten lead. If litharge is heated at 300 ^oC or so, it gradually transforms into red lead. Litharge can be reacted with vinegar to form the acetate, which then decomposes to form white lead. Both forms have been known and used since antiquity, with white lead as a paint pigment as well as a glaze constituent. The lead-oxide content can be as much as 60% for low-melting enamels, but a whole series of lead-alkali mixtures work well, firing at increasingly higher temperatures as the lead content is lowered. Other constituents that act as strong fluxes somewhat similar to lead are barium oxide (BaO), zinc oxide (ZnO), and bismuth oxide (Bi_2O_3), which is more expensive but is used in some low-melting enamels, particularly as a flux for gold decoration. Barium carbonate is used as a flux in stoneware glazes; raw glazes containing a lot of a zinc oxide are called *Bristol* glazes (Rhodes 1959; Kingery 1986; Rice 1987).

6.2.2 FRITTED GLAZES

If the available alkali is soluble – such as natron collected in the desert, calcined plant ash (sodium and potassium carbonates), or sea salt – it must be rendered insoluble by premelting it with silica for use as glazes that are to be mixed and milled. This is also true of borax and boron oxide. Fritting is now required to make heavy-metal poisonous constituents such as lead and barium nontoxic. To be insoluble, the amount of alkalis such as sodium and potassium should not be much more than half the total basic oxide content. The silica plus boron oxide should be one to three times the basic oxide content, so as to form a glass on cooling. A Current practice, and the one traditional in the Near East, is to completely melt the frit, and, when possible, pour it into water, which breaks it up into small particles suitable for milling. Early glass practice, beginning about 1500 BC, was to sinter the reactants together and react them in a partially molten state. This process continued in use for European maolica glazes and French soft paste porcelain. The two different processes have both been called fritting, and this has led to some difficulty in terminology – the French word *fritte* is best translated as 'sinter'. The fritted portion of the glaze is ground to a fine particle size together with insoluble 'mill additions' such as additional quartz to raise the glaze fusion temperature, clay to aid suspension, white lead (which also has good suspension properties), a tin-lead calcine to give opacity, colouring additives, and pigments. After milling the glaze is usually screened through a fine cloth to eliminate coarse particles (Kingery 1986; Atasoy and Raby 1989).

6.3 DECORATION TECHNIQUES OF POTTERY

6.3.1. SLIPS AND UNDERGLAZE DECORATION

Surface coatings that have a composition similar to that of the body are called slip coatings or engobes. The objective is to provide a smooth surface with a colour different from that of the underlying body and a good white ground for painting. The slip can be painted to furnish a design as in Neolithic ware that used clays containing high concentrations of iron (red), manganese (black), or chromite spinel (black). Designs can be added. Ceramic colours require careful preparation for successful results. The colouring ingredient, plus any added white pigment extender such as quartz or fired white clay or tin oxide, often mixed with a 20-30% frit or flux addition, were frequently baked or calcined together, and then remilled to from a more uniform mixture. Without such preparation the colours would appear blotchy and the intensity of colour and flow of the colour during application would be hard to control. Water-based paints with gums or glue added to furnish proper adhesion have been the traditional method. Oil media have also been used. In this case it is necessary to preheat the underglaze decoration to a red heat to eliminate the organic material before firing; otherwise bubbling of the colour will result (Rhodes 1959; Rye 1981; Rice 1987).

6.3.2. COLOURANTS, PIGMENTS AND OPACIFIERS

Coloured glazes and enamels can be formed by dissolving a small amount, usually between 0.5 and 4%, of the colouring oxide in the glaze. Copper oxide, for example, when dissolved in the alkaline glaze is a beautiful blue. However, copper oxide dissolved in a lead-silicate enamel is a clear green, whereas it imparts a turquoise colour to the lead-alkali-silicate glaze. Other common solution colours are iron, which in an alkaline glaze gives a light greenish blue but in a lead glaze is yellow or brown; manganese, which gives a purple colour; cobalt, which in alkaline or lead glazes gives a clear blue colour (but is green in high-potassium glazes); nickel, which gives rise to a gray tone; and chromium, which varies from colourless to green. In high-lime glasses containing appreciable alumina, copper oxide is green. The sensitivity of the surroundings to the colour produced means that minor constituents such as sulfur, fluorine, and carbon can also have a great effect (Weyl 1951; Rhodes 1959; Singer 1963; Noll et. all 1975; Rye 1981; Rice 1987; Constant and Oqden 2000).

Colours also vary with the state of oxidation or reduction of the glost firing. Colour is a bright blue in an oxidized alkaline glaze, but it becomes more greenish, and may even turn clear, as the firing is reduced slightly. Manganese is purple in oxidation but brown in reduction; iron in a low concentration is green in celadons or blue in jun ware. As the iron concentration increases, the colour darkens to brown and then turns to black, the degree of blackness depending on the glaze thickness. Colours of transparent or translucent glazes also depend on the colour of the underlying body; celadons that are green on a white body become olive or gray-green on a darker underlying body (Weyl 1951).

A quite different type of colour results from the precipitation of tiny colloidal particles of gold, copper, or silver in a reducing atmosphere. Tiny here means very small indeed, about 100 nanometers, or a millionth of a centimeter. When present in sufficiently fine particle size, copper and gold result in a red colour, where silver more often has a yellow tint. As the size of the particles increases, the colours become more purplish, then a livery brown. The most sensitive colourant is gold, of which only 0.01 weight percent is required; cooling and reheating give the best gold-ruby colour. Copper colloids are similar to gold, but a larger concentration is needed, 0.1 to 0.5 %. If the copper is present in small amounts, it forms copper metal particles and the transparent bright red colour is produced; higher concentrations tend to form copper oxide crystals, Cu_2O, which give a darker brick red (Weyl 1951; Parmelee 1973; Kingery 1986).

Many of the colourants used for glazes and enamels do not dissolve but rather function as pigment particles in the same way that pigments are used in paint. As most pigment materials dissolve at high temperatures, only a few can be used as underglaze colours in hard porcelain, whereas the range of colours available for low-firing enamels is much greater. Pigment’s ingredients are intimately mixed with a flux, often borax, which forms a liquid on heating to accelerate the reaction process. After the crystalline pigment is formed, the borate flux is removed by dissolving it in acid; the pigments then are milled to obtain the fine particle size necessary for effective light scattering. Widely used ceramic pigments have been lead antimonite (Naples yellow), chromium oxide (green), iron oxide (Fe_2O_3, red-brown), manganese oxide (black), iron oxide scale (Fe_3O_4, black), and chromite-ferrite spinels ($[MgFeAlCrTi]_3O_4$, black). White pigments such as tin oxide (SnO_2), arsenic oxide (As_2O_3), and calcium antimonite were used as opacifiers (Rhodes 1959, Rye 1981; Singer 1963). At the 18th century it was found a mixture of alkalis provided a more effective flux than any alkali alone. In addition to lead oxide as a flux, bismuth oxide, barium oxide, fluorspar (CaF_2), and especially borax and boric oxide, were widely employed (Weyl 1951; Parmelee 1973; Kingery 1986). The difference in the colours is that the pigments were calcined at different temperatures. For instance, the iron oxide, as the calcination temperature increases, the particle size of the pigment increases so that the resulting colour changes from a clear coral red to a brownish gray (Weyl 1951; Kingery 1986; Rice 1987).

The white pigments were used as opacifiers, but they also play a strong role in brightening colourants in solution by providing diffuse reflection of light back to the surface. Tin oxide has been by far the most widely used white pigment, as it is easy to prepare in fine particle size by oxidation of a lead-tin mixture, is insoluble, and has a high refractive index. Tin oxide dissolves in higher temperature glazes, as do other effective opacifiers, so that dense, white, opaque porcelain glazes are not possible. In high-lime glazes, opacity results from calcium silicate ($CaSiO_3$) precipitation if cooling is slow. White bodies may be opacified or coloured with stains by adding up to 10% of pigment and thoroughly milling to achieve uniformity and avoid mottling. As the temperature is increased above about 1100 ^oC, firstly the iron oxide gives a darker colour due to a partial reduction, after becoming a chocolate brown and then transforming to black magnetite, Fe_3O_4, at 1400 ^oC in air. In more reducing atmospheres, this transformation occurs at lower temperatures, so that ware fired with a smokey flame is gray and then black at temperatures as low as 500-600 ^oC (dull red heat). Brick and terra-cotta colours are much affected by other constituents as well, with calcium oxide in the clay giving a buff colour, and manganese impurities resulting in brown (Tables 11,12, 13) (Rhodes 1959, Singer 1963; Rye 1981; Rice 1987; Fitch 2003).

Thus, we see that several variables affect the final colour achieved. These include (1) the number and concentration of colourants, (2) the amount and type of opacifier or pigment particles, (3) the size of the pigment particles, (4) the composition of the glaze, (5) the state of oxidation or reduction of the colourant, and (6) the presence of small amounts of constituents such as carbon and sulfur that react with the primary colourant to form compound 'chromophores'. Even though there are only a few basic colourants, the opportunities for subtle and not-so-subtle variations are staggering (Kingery 1986, Constant and Oqden 2000; Fitch 2003).

6.3.3. OVERGLAZE DECORATION, ENAMELS, GILDING AND LUSTER

In the twelfth century, during the Song Dynasty ware of China and the Mina'i ware of Persia, pigments were added to low-temperatures fluxes for painting on the surface of glazed ceramics, which were then refired to fuse the applied decoration. The overglaze enamel became an integral part of the glaze surface. The method was widely used in both China and the Near East during the 15th century. The porcelain body increasingly became a white ground with more and more focus on the overglaze painting. At this time in Europe there was also a change from maiolica painting techniques to overglaze enamels. Lusters as an overglaze painting medium had been in use since the 10th century in the Near East. The simplest low-melting enamel flux consisted of a finely milled mixture of 25% quartz sand and 75% white lead. Colourants such as cobalt oxide or copper oxide, which enter into solution in the enamel, were added and the enamel ground wet with mortar and pestle (Weyl 1951; Parmelee 1973; Kingery 1986; Fitch 2003).

Particularly for copper colours, to achieve a range of green tones, saltpeter (potassium nitrate) was used, which required fritting the enamel to avoid efflorescence. When iron oxide was used as a pigment, the alumina content was increased to give a brighter red (Tables 13). European practice, beginning in the early 18th century, almost always included some boric oxide or borax as an ingredient to make a low-melting lead borosilicate. A typical formula consisted of 67% white lead, 22% quartz sand, and 11% fused borax. Fluxes were melted with copper or cobalt to form greens and blues, but increasingly, as applied chemistry developed new stains, insoluble pigment particles were added to the flux in amounts ranging from 10 to 20%, and milled to form a fine, uniform composition. Following the practice of painters, European enamellists mostly used an oil-turpentine medium. During the 18th century, the range of colours available increased enormously (Weyl 1951; Rhodes 1959; Parmelee 1973; Kingery 1986; Constant and Oqden 2000).

For complex designs and elaborate symmetrical decoration, the designs, before being painted, would be outlined with a dye or with powdered charcoal sifted through a perforated paper. The lead silicate or lead borosilicate enamels vitrify and react with the glaze at a temperature of 650-700 ^{o}C, which is easily achieved with muffle kilns in which the setting space is separated from the combustion flames. For gilding, the cheapest method is to incorporate soluble gold salts in a varnish; firing in a reduction atmosphere at about 700 ^{o}C forms a thin layer of metallic gold, but the adherence is not particularly good. Thicker, richer gilding is done by mixing powdered gold metal with a low-temperature flux, frequently bismuth oxide, and firing at about 700 ^{o}C to form a brownish colour. Burnishing causes the soft metal to flow into a continuous polished layer (Rhodes 1959; Constant and Oqden 2000).

6.4 FIRING OF THE GLAZES

For most stoneware and hard porcelain, the glaze is applied to the unfired ware, but sometimes a low-temperature biscuit firing precedes the glaze application. In both cases the glaze and the ware are matured together in the highest temperature firing. High firing of glaze and body together causes some of the molten glaze to penetrate into the body and produces a reaction layer that greatly improves adhesion. Some body dissolves in the glaze; there is usually an enrichment of alumina and the formation of anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) or mullite ($3Al_2O_3 \cdot 2SiO_2$) crystals at the interface. Most semi-vitreous ware, soft-paste porcelain, and bone China undergo two firings. The glaze is applied to pre-fired biscuit. The most common glaze compositions are lead-alkali-silicate, lead-silicate, and lead-borosilicate. In enamels applied over glazes, melting occurs at such a low temperature that the refractory pigment particles are not dissolved. The firing must be fast enough that there is no reaction between glaze and enamel and that the enamel does not spread over the glaze surface. Finally, if cooling is slow, cristobalite or tridymite crystals may form at the glaze surface, resulting in a rough velvety surface and reduced transparency. Matte glazes are compounded with a high alumina content, which, together with calcium or barium, forms crystals at the surface to give diffuse reflectivity and a velvety sheen. The most common crystals are the calcium or barium feldspars ($CaO \cdot Al_2O_3 \cdot 2SiO_2$, $BaO \cdot Al_2O_3 \cdot 2SiO_2$) and wollastonite ($CaSiO_3$), but sometimes mullite ($3Al_2O_3 \cdot 2SiO_2$) appears (Rye 1981; Kingery 1986; Rice 1987).

6.5 THE FLUX K VS NA

Medieval European glasses contained calcium and potassium in addition to silica. 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. The 11th c. Benedictine monk, Theophilus Presbyter, to whom we owe one of the most analytic descriptions of Medieval art, namely *Schedula diversarum artium*, gave 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). On the other hand, opaque (non-transmitting) glasses from northern Medieval Europe contained a 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 coloured stones" (Roman glass). The role of potassium or sodium in glass is that 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 (Fayon et al. 1994). Ashes, a source of either potassium or sodium were often used in the early glazes. Potassium or sodium can inhibit the glass chain rupture and 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 (Figure 85). 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. Because Na has a smaller ionic radius and 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] 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). 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 $\sqrt{(3.25)}$ (Fitch 2003).

6.6 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 nonbridging oxygen in the silica backbone. Pb^{2+} acts like K^+ or Na^+ to stabilize Si chain breakage. Lead chains can arise from αPbO (red lead, with a tetragonal pyramidal structure, Figure 86) with equidistant (2.31 Å) Pb-O bonds or it can come from $_{\beta}$PbO (orthorhombic structure, Figure 87) 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_3O_4 (Figure 88) (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; Stemmermann et al. 1991; Fitch 2003). 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). We can approximate the structure of leaded glass if we start with a model for the structure of the mineral pyromorphite (Stemmermann et al. 1991). A similar model can be proposed for lead silicate glass. The PbO side chains help stabilize breaks in the SiO4 tetrahedral chain and thus keep the directionality of bonding while breaking the three-dimensional network. The proposed model assumes a structure of $[Pb_{40}(Si_2O_7)_6(Si_4O_{13})_3]O_7$. Others have concurred with the hypothesis of PbO_4 pyramids intercalated within Si di-tetrahedra ($Si_2O_7^{6-}$) (Hill 1985; 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).

6.6.1 LEAD AND OPACIFIERS

White opaque glass contains lead and tin. An opacifier is a substance that does not impart colour and that has a large particle size 0.35 μm to 1 μm (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 colour-forming range. SnO_2 crystals reflect light back without absorbing any particular wavelength and consequently appear white. 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 20-30μm 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. 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 $Pb_2(AsO_4)_2$ and $Pb_3(PO_4)_2$. 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. Similarly, lead forms a PbSb compound that imparts a yellow colour to the glass (Fitch 2003).

6.6.2 LEAD AND BRILLIANCE

One of the desirable properties of glass is its shine. 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] $\alpha_v = (3M/L\rho)\,(n_r^2-1)/(n_r^2+2)$
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 nr is the refractive index of the material.

The higher the number of electrons and the weaklier they are held, 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.

A high refractive index means that at a metal/air interface, light is highly reflected, resulting in a shinier surface:
[4.3] $I_R/I_o = (n_2 - n_1)^2/(n_2 + n_1)^2$
where IR/Io is the ratio of light reflected to original light and n is the refractive index of the material.

As the refractive index of some elements as FeO deviate, the modified term 'molar refractive index' is:
[4.4] $R_m = [M (n^2-1)]/[(n^2+ 2)d]$
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. The metal oxide density affects 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. 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:
[4.5] $(Si(O_{1/2})_3O^-)R \rightarrow Si(O_{1/2})_3O^- + R^+$
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: $CaO<SrO<Li_2O<BaO<Na_2O<K_2O$. This basicity trend suggests why lead makes glass more brilliant. Lead is quite low in charge density because of its $d^{10}s^2$ 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 (Fitch 2003).

6.7 CLAY AND TEMPERATURE

Back in 1995, Guggenheim and Martin expressed the view that clay classification was formalized in 1546 by Giorgio Agricola. The Joint Nomenclature (JNC) of AIPEA and the Clay Mineral Society have defined clay as "… a naturally occurring material composed primarily of fine-grained minerals, which generally gets plastic at appropriate levels of water contents and will harden when dried or fired". The ample component is the clay matrix; most clay fabrics usually contain more than 50% of clay matrix. Clay minerals within the clay matrix allow plasticity, as their thin, sheet-like shapes of aggregations serve to attract and hold water between their surfaces.

Several scientific methods attempt to estimate the temperature at which a clay object has been fired. These methods examine either mineralogical changes which occur during firing or on colour changes or, eventually, on sintering and vitrification. However, defining the firing temperature is not always easy, as the results are affected by the firing rate, the soaking time and the duration of firing. Therefore, several researchers (Norton and Hodgdon 1931; Shepard 1956; Maniatis 1976; Maniatis and Tite 1981). The mineralogical and chemical transformation of a clay raw material during firing (particularly in low temperatures, i.e. 700-1100 ºC) depend on the composition and particle size of the given material, the maximum firing temperature and atmospheric conditions in the kiln as well as on the soaking time (Cultrone et al. 2001).

Many researchers studied the mineralogical and textural modifications during firing due to the presence of carbonate or non-carbonate mixtures in the clay paste (Bohor 1962; Tite and Maniatis 1981; Freestone and Middleton 1987; Veniale 1990; Jordan et al. 1993; Duminico et al. 1997; Riccardi et al. 1999; Rye 1976; Peters and Iberg 1978; Maggetti 1982; Capel et. al. 1985; Gonzalez-Garcia et al. 1990; Cultrone et. 2001). These studies provide significant evidence of temperatures, mineral reactions and textural transformations. The reactions that occur during firing between the clay micromass and clastic minerals (e.g. quartz, feldspars) are classified in two mechanisms: a) reactions that lead to the crystallization of new mineralogical phases (modal reactions), and b) reactions which cause only compositional changes in the phases (cryptic reactions) (Riccardi et al. 1999). The creation of new mineral phases is determined by dehydration reactions and the release of CO_2 (decarbonation). The decomposition of the clay minerals and calcite result in the evolution of the fluid phases of H_2O and CO_2 respectively (Duminuco et al. 1997). In clays with a high density of CaO, the decomposition of calcite (around 750 °C) results in the production of CO_2 at 12 wt% (Duminuco et al. 1997).

The microtextural and microchemical correlations between mineralogical phases during firing result from the transformations within the clay paste, from the primary mineralogical phases and from the distance between the clay paste and the clay minerals. A ceramic entity undergoes the following modifications as the firing temperature goes up:

- The clay matrix and clastic grains are progressively sintered.
- The mineral shape is changed.
- The interior of the micromass is increasingly aggregated and secondary porosity is created.
- The grains are strongly connected, porosity is decreased with the growing of the glassy phase and textural and chemical characteristics tend to become more homogeneous (Riccardi et al. 1999).

6.8 VITRIFICATION

During the heating of clays various forms of solid-state reactions take place that yield the new phases. The silica from the crystal lattice reacts with fluxes such as Na_2O, K_2O, CaO, MgO and FeO, which are provided mostly by the accessory minerals in the clay body to form a ‘liquid phase’ which on cooling does not crystallize but solidifies to form an amorphous phase (glass). In the presence of the liquid phase sintering of the clay particles occurs which results in the densification of the clay body. It is now known that the sintering of clays during firing occurs with the transfer of material to the contact surface between the particles through a process of ‘plastic flow’ (mobilization of molecules without full melting) (Kingery et al. 1976). The process of sintering in the presence of a ‘liquid phase’ is known as vitrification. The development of a glassy phase (vitrification) is independent of the sintering (Table 14).

The vitrification occurs in association with the breakdown of the crystal lattices and it can start in a clay below 900 °C. The end of the vitrification period is frequently defined as the highest temperature which the clay product can survive without distortion, and this can be as low as 1100 °C for an easily-maturing, low refractory clay or as high as 1600 °C for a China (high refractory) clay (Grim 1968; Rice 1987). Vitrification appears as continuous glass filaments at first, joining the edges of the parallel aligned clay particles and later as wavy glassy strips when the filaments from several clay layers fuse together. Depending on the chemical and mineralogical composition and the particle sizes variations may occur regarding (i) the temperature at which the aforementioned changes take place, (ii) the amount of glassy phase which is developed, (iii) the pattern which the vitrification creates in the clay matrix, (iv) the degree of pottery contraction (Maniatis 2009).

The calcareous ceramics, containing CaO>6% in a fine calcium carbonate form, exhibit a characteristic cellular structure with a high porosity (Tite and Maniatis 1975) and in the same time the vitrification is more restricted and controlled up to 1150 °C. This characteristic microstructure remains constant for 200 °C (850-1050 °C) and above that there is a progressive increase of vitrification. The degree of vitrification is inhibited due to the crystallization of the newformed calcium phyllosilicate phases (anorthite, gehlenite, wollastonite, diopside) which present a rather high melting point. Vitrification is affected mainly by the sufficient amounts of calcium required for the crystallization of new phases and/or to the fine grain size of calcite and its uniform spatial distribution within the clay matrix are likely the main factors affecting the vitrification. The uneven distribution of calcium has as a result the non-well-developed of the vitrification and at the same extent across the ceramic surface. If the percentage of CaO is over 10 wt.%., the degree of vitrification does not remain stable in the temperature range of 850°C and 1050 °C, but there is a slight increase of the glassy phase. When the temperature exceeds 1050 °C, the vitrification is increased rapidly, whereas coarse unconnected pores are formed. The glass phase becoming grainy and highly viscous. Contrary to that, the non-calcareous clays, containing CaO<6%, produce a much more vitrified ceramic body with a high density and impermeable to fluids. Furthermore, due to the extensive and rapid vitrification the non-calcareous ceramics collapse at temperatures approaching 1100 °C (Tite and Maniatis 1975; Maniatis 2009). Non-calcareous clay martial givers ceramics whose sole high temperature crystalline phase is the spinel, detected in small amounts. The rise of temperature results in the isolated glassy areas associated with the initial stage of the vitrification to steadily increase in size until they join and form a smooth vitrified area. The initial stage of vitrification from the state of continuous vitrification are some 150 °C apart. In calcium-rich clay pastes, the microtextural characteristics during firing are more evident and are created at lower temperatures (~850 °C) than those recorded in the case of low calcareous pastes. As the latter undergo firing, the texture of the clay mass is re-arranged in temperatures beyond 1050 °C, coupled by the complete breakdown of the clay minerals (Veniale 1990; Dondi et al. 1998a,b; Duminico et al. 1997).

If atmosphere inside the kiln is reduced, a variety of vitrified structures are formed during the temperature increase and in a range of 50 °C. The rapid development of the vitrified areas in conditions of reduced atmosphere is in accord with the low CaO content (less than 6%), determined by chemical analysis. The stable mineral phase in that case is fayalite, vitrified at low temperatures. In oxidized conditions and at high temperatures, the crystalline phase is the ferrous spinel (Muan 1957; Naslund 1976). On the other hand, small pores appear in high amounts when the temperature of vitrification is low and the atmosphere is high. When the firing temperature increases, these pores increase as well, whereas their number decreased as they tend to be associated with the largest spherical pores and ultimately be connected to the final stage of vitrification (Maniatis and Tite 1981). To sum up the stages of vitrification are summarized in the Table 14 (Noll 1991; Tite et all 1981; Tite and Maniatis 1975a,b; Tite 1969).

Finally, the calcareous ceramics are more resistant to thermal and mechanical shocks due to their highly porous microstructure which absorbs energy, but they have lower resistance to loading and compression, as they are less rigid. The mechanical and thermal properties of ceramics can be modified strongly by introducing aplastic inclusions whose concentration and size affects strongly these properties. Such inclusions may be fragments of quartz, feldspars, limestone, seashells etc. (Grim 1968; Kingery et al. 1976; Rice 1987).

6.8.1 BLOATING

With progressive heating of an already vitrified clay body, the amount of glass and the sintering increases and at the same time the viscosity of the glass decreases. The process continues until a temperature is reached where the amount of gas released from the chemical reactions and the glass viscosity is such that spherical pores are formed in the ceramic body. This phenomenon is called bloating and the temperature at which it appears depends on the particular clay and the atmosphere during firing. In general, for low refractory clays in an oxidizing atmosphere it may start at about 1100 °C and in a reducing at temperature as low as T 900 °C. Once bloating has started usually it increases in pore-size with increasing temperature and the body swells and becomes very porous (Maniatis 2009).

6.8.2 COLOURS OF BODY AND PAINT IN OXIDIZING CONDITIONS

It is known that the colour exhibited by a ceramic is a result of the chemical composition of the clay and the firing conditions (temperature and atmosphere). The iron oxides play a very important role in the final colour of the fired ceramic and influence also the colour of the natural raw clay. Initially iron is in the form of iron hydroxides within the raw clay. For example this happens with FeO(OH), orange or brown in colour, and fine iron trioxide (Fe_2O_3), which is red/brown in colour. Some Fe is also bound in the form of ions Fe^{3+} or Fe^{2+} in the structure of the clay minerals that are colourless. The combination of the different forms and quantities of iron existing in a clay together with the quantity of organic material contained gives a variety of colours to the raw clays, ranging from grey, beige, brown, orange, or red (Maniatis 2009).

Upon firing, the colours of clay change depending on the temperature and atmosphere, but the presence of fine calcium carbonate in the raw clay affects the final colour, as in the development of micromorphology. In non-calcareous clays fired at oxidizing atmosphere there is a progressive crystallization of Fe in the form of alpha-Fe_2O_3 (hematite), which is red in colour. These oxides grow in size and quantity as the firing temperature increases above 700 ^oC at the expense of the Fe-hydroxides and the Fe-ions in the clay mineral lattice, which begin to disorganize and dissociate above that temperature liberating Fe ions (Maniatis 2009). As a result, the non-calcareous clays fired at oxidizing atmospheres tend to be red-coloured, and their reddish shades become more intense as the firing temperature increases. Contrary to that, the reactions occurring during firing in the calcareous clays (fine CaO>6%) are quite different. The CaO that appears from the dissociation of calcium carbonate above about 750-800 ^oC, reacts strongly with the iron oxides and breaks them down. This leads to the decrease in the size and amount of Fe-oxide particles and hence to the bleaching of the red colour to pink, cream or even whitish as the temperature increases above 850 ^oC and according to the original amount of calcium carbonate in the clay. The Fe which is liberated from the dissociation of iron oxides induces the crystallization of new calcium aluminosilicate minerals which stabilize the microstructure of the calcareous clays for 200 ^oC (850-1050 ^oC). These new minerals are colourless (Maniatis et al. 1981; Adams 1985).

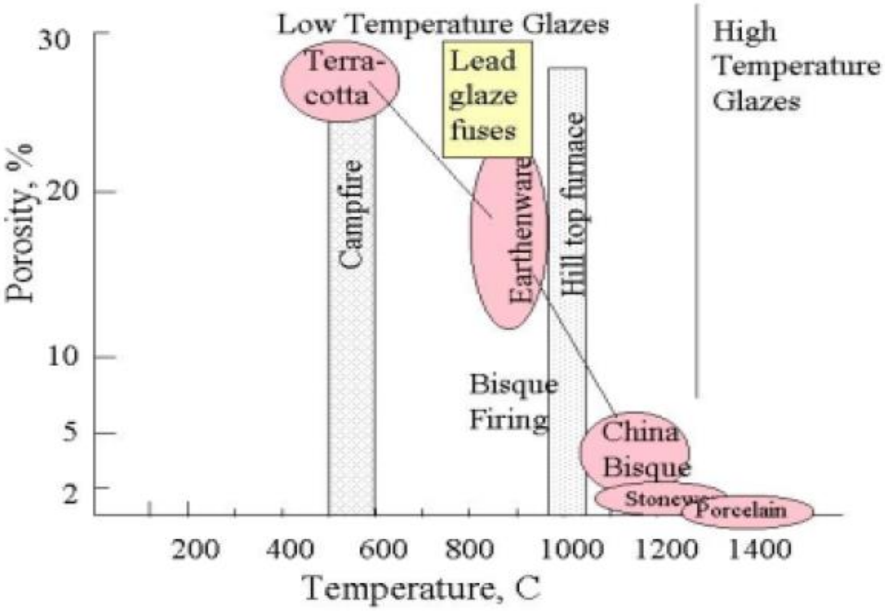


Figure 82 Porosity decreases with temperature. Very high temperatures are needed to remove the water from clay to achieve porcelain (Fitch 2003, p. 165).

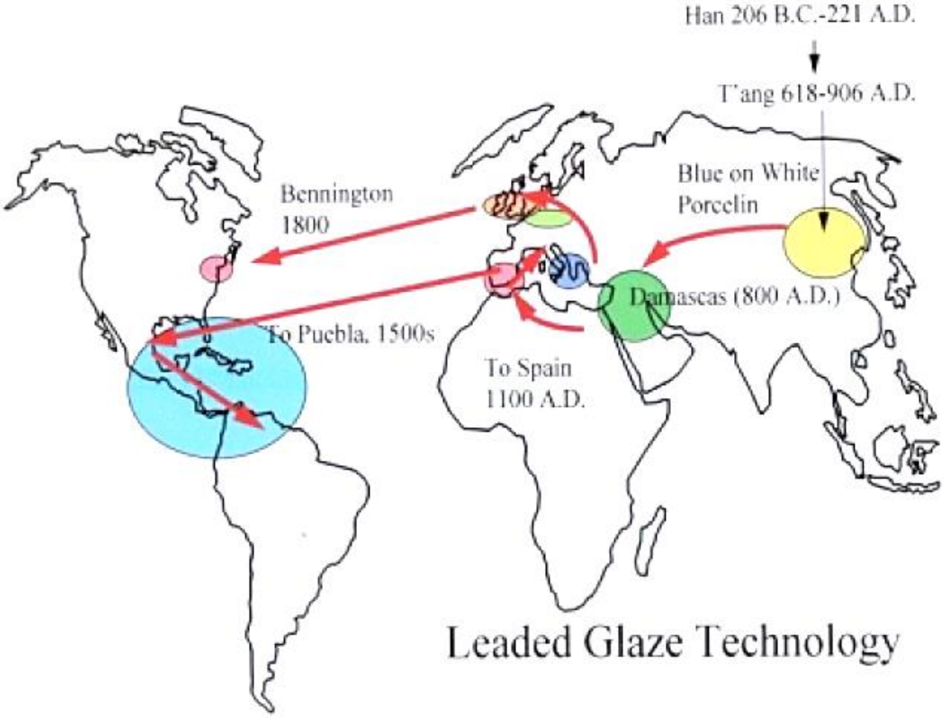


Figure 83 The spread of the lead glaze technology (Fitch 2003, p. 172).

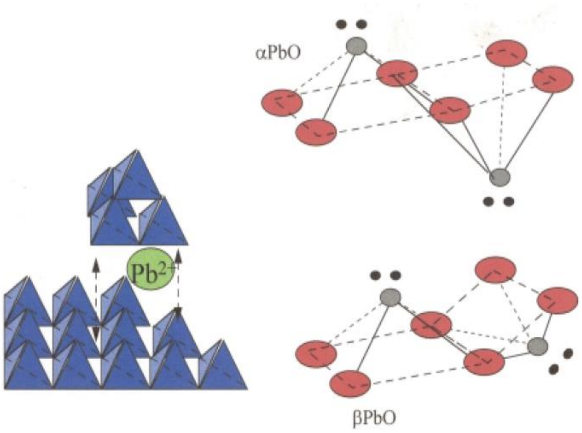


Figure 84 Lead reduces the temperature for working with glass by enhancing fluidity by stabilizing breaks in the glass chains (left) and by providing lead oxide chains to link glass subunits (Fitch 2003, p. 148).

The glaze melting temperature depending on the participation of its oxides	The viscosity of fired glaze in relation to the participation of oxides in its composition
Al_2O_3 SiO_2 MgO Cr_2O_3 SnO_2 ZrO_2 NiO Fe_2O_3 Sb_2O_3 TiO_2 CaO ZnO BaO SrO FeO CoO CuO MnO PbO B_2O_3 Na_2O K_2O Li_2O ↑ The glaze melting temperature increases with the participation of these oxides in its composition. ↓ The glaze melting temperature decreases with the participation of these oxides in its composition.	Al_2O_3 ZrO_2 SiO_2 Cr_2O_3 SnO_2 NiO Fe_2O_3 TiO_2 CaO MgO ZnO SrO BaO CoO MnO PbO K_2O Na_2O B_2O_3 Li_2O ↑ As the oxides participation increased; the viscosity also increased. ↓ As the oxides participation increased; the viscosity also decreased.

Table 10 The effect of oxides on the eutection and viscosity of glazes (Matthes 1985).

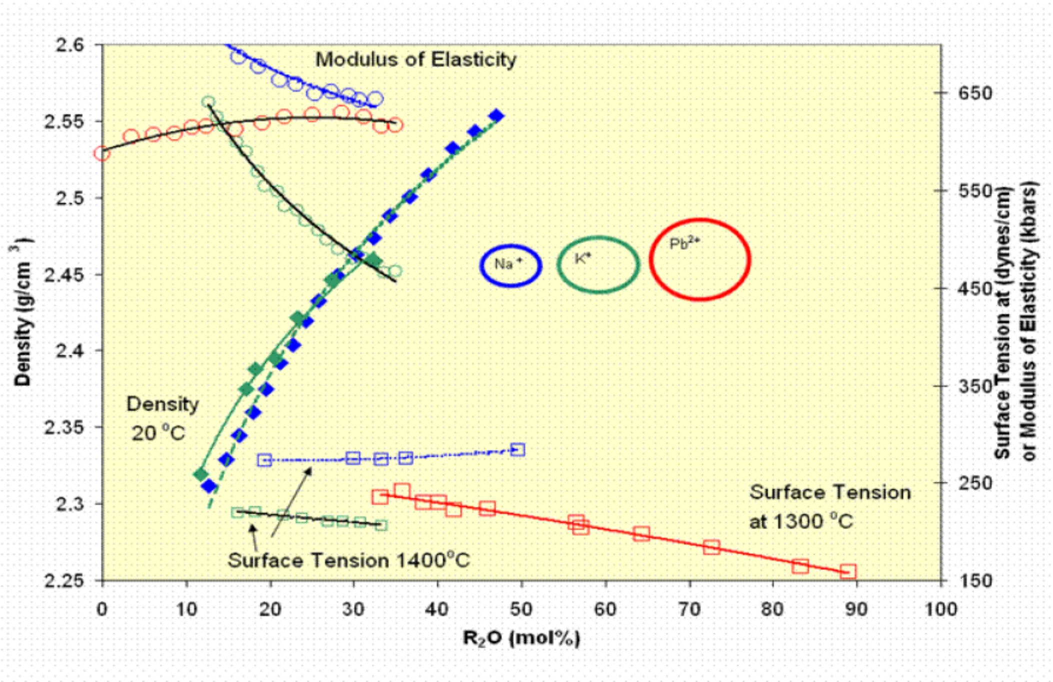
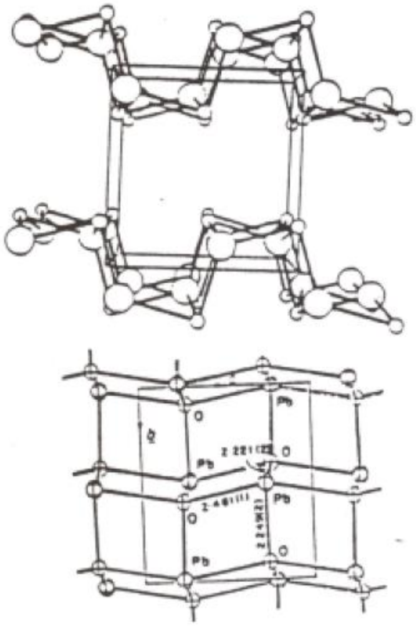


Figure 85 The density of glass modified with K, Na; the surface tension of glasses modified with K, Na, and Pb; and the surface tension of glasses modified with K, Na, and Pb (Fitch 2003, p. 183).



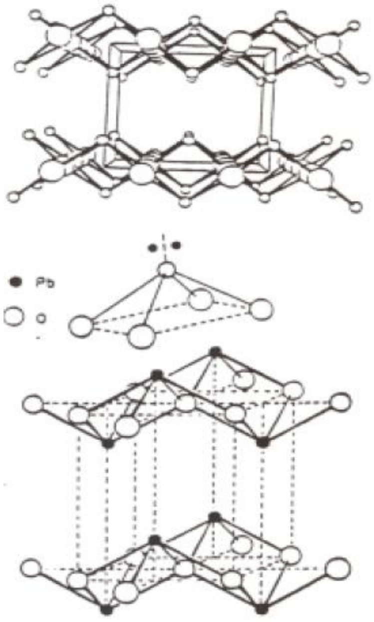


Figure 86 $_{a}$PbO, tetragonal known as litharge or red lead (Wells 1984; Fitch 2003, p. 184).
Figure 87 $_{\beta}$PbO, orthorhombic, also known as massicot (Wells 1984; Fitch 2003, p. 185).

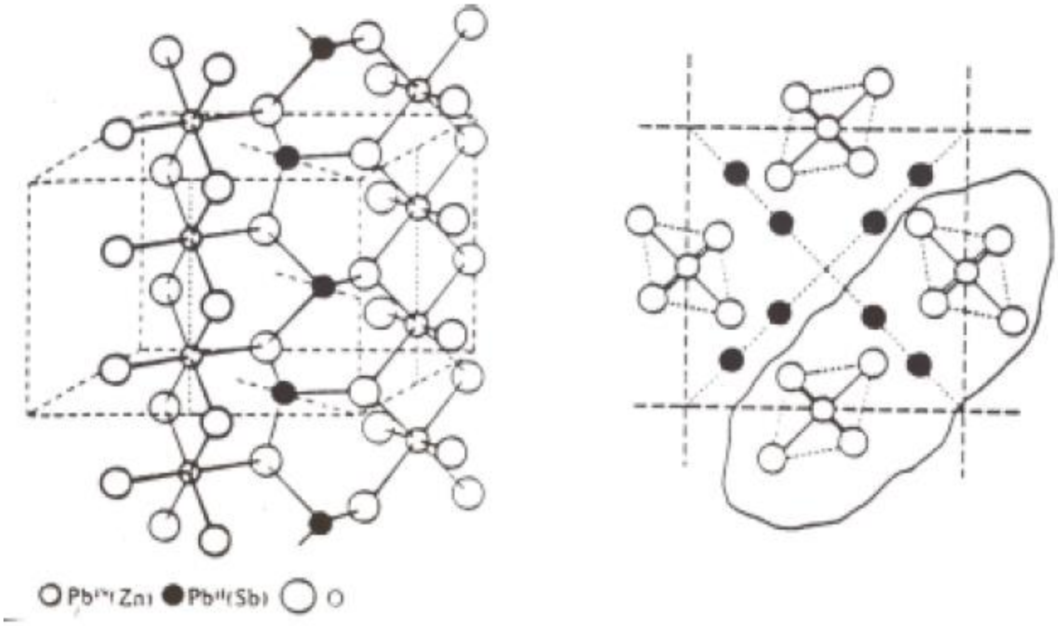


Figure 88 Structure of minium, Pb_3O_4, (Wells 1984; Fitch 2003, p. 186).

PIGMENT COMPOUNT	**FIRING TEMPERATURE**	**KILN ATMOSPHERE**	**GLAZE COMPOSITION**	**% COLOURANT CONTENT**	**OBSERVATIONS**
BLUE					
COBALT OXIDE	At all temperatures	Oxidation or Reduction or Neutral	Glasses rich in ZnO	0,05-2% CoO	In glasses rich in MgO and TiO_2 the colour acquires a violet or greenish hue respectively. In barium glasses, the CoO must be used in small quantities.
COPPER OXIDE	At all temperatures	Neutral to Oxidation	Glazes rich in alkali, but low in Al_2O_3	1-4% CuO	The presence of oxides PbO, Al_2O_3, ZnO, TiO_2, prevents the growth of the blue colour.
NICKEL OXIDE	At all temperatures	Neutral to Oxidation	Zinc matte glass (ZnO)	1-4% NiO	In crystal glasses, ZnO-SiO_2 crystals are coloured blue to green-blue by Ni ions.
TITANIUM OXIDE	Above 1150 ºC	Reduction to Neutral	All lightly reduced glasses	4-10% TiO_2	The presence of ZnO and SnO_2 favors the development of blue. The development of colour seems to be favored by rapid cooling.
BLACK					
MANGANESE OXIDE	At all temperatures	Oxidation or Reduction	All glasses	6-30% MnO_2	In large quantities of MnO_2, the glass must be dilute.
IRON OXIDE	Above 1190 °C Up to 1100 °C	Reduction Oxidation	Feldspar glasses Lead glasses	8-15% Fe_2O_3 15-20% Fe_2O_3	A large amount of SiO_2 is needed.
COPPER OXIDE	At all temperatures	Oxidation	All glasses	8-12% CuO	Black metal
MIXING OF OXIDES $CoO+CuO+MnO_2+Fe_2O_3$	At all temperatures	Oxidation or Reduction	All glasses	Mix up to 15% in equal percentages	

Table 11 The pigments of the glazes (Matthes 1985).

PIGMENT COMPOUND	FIRING TEMPERATURE	KILN ATMOSPHERE	GLAZE COMPOSITION	% COLOURANT CONTENT	OBSERVATIONS
GREEN					
COPPER OXIDE	At all temperatures	Oxidation	In lead glasses and in many matte glasses	1-5% CuO	At high temperatures CuO evaporates. The high content of CuO gives metallic black.
CHROMIUM OXIDE	At all temperatures	Oxidation and or Reduction	At all glasses except for ZnO glasses	1-5 % Cr_2O_3	In rich alkali glasses the Cr_2O_3 should be more than 2%, in rich lead glasses green colour does not exist below 1000 ºC.
IRON OXIDE	At all temperatures At all temperatures, but especially at high temperatures	Reduction and rapid coolling Oxidation	Glasses with CaO-B_2O_3 and rich in MgO	0,2-2% Fe_2O_3 1-3% Fe_2O_3	Quick cooling to avoid re-oxidation of Fe. Deep oily green.
NICKEL OXIDE	At all temperatures	Oxidation	Glasses with rich content of TiO_2 and MgO	1-5% NiO	Better results in matte glasses.
COBALT OXIDE	Above 1150 °C	Oxidation	Matte titanium glasses	2-4% CoO	B_2O_3 is necessary for better colour development.
CADMIUM SULFIDE & IRON OXIDE	Up to 1150 °C	Oxidation	Alkaline glasses	0,5-2% Fe_2O_3	
COBALT OXIDE	At all temperatures	Oxidation and or Reduction	At all glasses that contain ZnO	0,05-2% CoO	Glasses that contain enough MgO and TiO_2 produce violet blue. Glasses that contain enough ZnO and BaO, they need very little CoO.
COPPER OXIDE	At all temperatures	Oxidation	Alkaline glasses poor in Al_2O_3	1-4% CuO	The presence of PbO, Al_2O_3, TiO_2 undermines the cyan hue.
NICKEL OXIDE	At all temperatures	Oxidation	Matte glasses with Zinc	1-4% NiO	
TITANIUM OXIDE	Above 1150 °C	Reduction		4-10% $T\iota O_2$	ZnO and SnO_2 contribute to the development of the blue hue.

Table 12 The pigments of the glazes (Matthes 1985).

PIGMENT COMPOUNT	FIRING TEMPERATURE	KILN ATMOSPHERE	GLAZE COMPOSITION	% COLOURANT CONTENT	OBSERVATIONS
RED					
IRON OXIDE	Up to 1100 °C 1200°C to 1280 °C	Oxidation to neutral Oxidation or Reduction	Alkali-borate poor in Al_2O_3 Lead poor in B_2O_3 Alkaline – alkaline earth with MgO	5-15% Fe_2O_3 5-10% Fe_2O_3	Cooling in oxidizing atmosphere, low content of Li_2O, P_2O_5 in glass, develops colour better.
CHROMIUM OXIDE	Up to 1070 °C	Oxidation	Very rich in lead and poor in Al_2O_3, B_2O_3	1-6% Cr_2O_3	Especially in low temperature lead glasses 880 ^{o}C to 940 ^{o}C, in the presence of SnO_2 orange red hue is produced
COPPER OXIDE	At all temperatures	High Reduction	At almost all glasses	0,4-2% CuO	SnO_2 contributes positively to colouring
NICKEL OXIDE	1120°C to1270 °C	Oxidation	Only in matte glass containing barium and zinc	2-4% NiO	Slow cooling is necessary
GOLD CHLORIDE	At all temperatures	Oxidation to slightly reduction		0,3-1% $AuCl_3$	Slow cooling
URANIUM OXIDE	Up to 1080 °C	Oxidation	Very rich in lead	2-10% UO_3	Used sparingly (due to radioactive character)
CADMIUM AND SELENIUM OXIDE	Up to 1150 °C Up to 1260 °C	High Reduction Oxidation	Lead-free, alkaline-rich All glasses	Stains Cd and Se 4-15%	

Table 13 The pigments of the glazes (Matthes 1985).

Stages of vitrification	**Temperature (^oC)**		
	Calcareous clays	**Low Calcareous clays**	**Too low Calcareous clays**
No vitrification	< 800	< 800	< 950
Initial vitrification	800-850	800-850	950-1000
Extensive vitrification	850-1050	850-900	1000-1050
Intermediate	1050-1150	900-950	1050-1100
Total vitrification	> 1150	> 950	> 1100

Table 14 Stages of vitrification (Noll 1991; Tite et all 1981; Tite and Maniatis 1975a,b; Tite 1969).