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## **Chapter 10.6 Glazes and enamels**

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### **Abstract**

In the form of glazes and enamels, thin glass coatings are deposited on pottery, glass and metal surfaces for aesthetic reasons and also to tighten porous bodies and harden their surfaces. In this chapter, the preparation, composition, coloration, thermal expansion, micro- and nano-structures of these glass coatings are first surveyed. Attention is in particular paid to the optimization of thermal expansion matching upon cooling and heating, wetting properties and softening temperatures. In addition, the thinness of the coatings requires specific colouration techniques by pigments or metal nanoparticles, which is why a very large variety of compositions had to be used throughout the ages. The history of coatings on metal (Celtic, Limoges, and Chinese *cloisonnés* enamels), on glass objects (Roman/Ptolemy to Mamluks and then Renaissance) and on potteries (*terra cotta*, stoneware, fritware, and porcelain) is then reviewed along with their preparation routes (ashes, rocks) and compositions. Technical exchanges, as well as the different techniques used to obtain similar visual effects are addressed with emphasis on the most innovative productions including Tang/Yuan/Song porcelain, Abbasid/Fatimid lustre pottery, Chinese/Vietnamese stoneware and *celadons*, Japanese *Raku*, Iznik fritware, and European soft-, hard- and hybrid-paste porcelains. The chapter ends with the 19<sup>th</sup> century technical revolution, the Craft and Japonism movements and modern/contemporary production.

## 1. Introduction

Glass has long been highly valued in the form of thin layers termed *enamel* or *glaze* depending on whether the substrate on which it is deposited is smooth (*e.g.*, metal, glass) or porous (*e.g.*, porcelain). From Egypt, Phoenicia and Mesopotamia to the Indus Valley, glazed artifacts date back to about 2000–1500 B.C. [1]. There is actually evidence that bulk glass was a by-product of glazes, once the great aesthetic and practical value of the new material had been acknowledged in the Middle East (Ch. 10.2). Such coatings were used not only for decoration purposes (Fig. 1) but also for tightening a porous body and hardening its surface, which made for instance possible to keep safely liquids or other substances in large pottery vessels. In the Western world the first enamels date back to at least 1500 B.C. in Cyprus [2] whereas a older written mention of an enameled shield is found in the *Iliad* (8<sup>th</sup> B.C.). From diverse areas, famous artifacts include an 11<sup>th</sup> century B.C. enameled bronze wine ladle from the early Western Zhou dynasty (British Museum) or numerous Celtic enamels on brass, bronze, gold and iron made from at least the 4<sup>th</sup> B.C. with blue, red, green, yellow and black hues [3]. As to *millefiori* enamels, they appeared in Ireland during the 7<sup>th</sup> century A.D.

Since then, a great many new applications have been designed, ranging from porcelain or glass isolators coated with iron oxide-rich enamels to improve the electrical insulation of wire supports in wet atmospheres [4] to the development of advanced ceramics such as particular dielectric passive components (*e.g.*, capacitors, substrates, sockets, *etc.*) that are at the roots of the development of microprocessors and computers. Glazes are also deposited on alumina electronic substrates to be used in standard or harsh conditions [4] whereas, following a tradition originating in the glazes deposited on stone in ancient Egypt [1], enameled lava remains used in contemporary building décor.

Regardless of their functions and of the possibly complex shapes of their substrates, the deposited glass layers must not exhibit any puddle but have a constant thickness. Hence, it is obvious that enameling and glazing technologies involve much more than the preparation and firing of glass compositions. Without trying to deal with all varieties of enamels and glazes, this chapter will review their current preparation and the technical constraints exerted in particular by thermal expansion matching, describe the most pertinent innovations regarding composition and color, and finally present an overview of the history of enamels and glazes.

In preamble, some definitions are in order: *stoneware* designates non-porous pottery or ceramics fired at temperatures higher than 1200°C; *fritware*, pottery in which some ground glass has been mixed with the starting clay and sand material to promote partial melting upon firing to cement the grains with the molten frit; *porcelain*, various kinds of white wares that share a common vitreous surface and a non-porous body as first made from 3000 to 1500 B.C during the Chinese Shang and Shang-Zhou dynasties (in the form of proto-porcelains, which were already fired up to about 1200–1250°C) [5]; *celadon*, a green Chinese porcelain as named in France in the 17<sup>th</sup> century; and *cloisonné* and *champlevé*, enamels prepared with two different kinds of techniques.

## 2. Preparation and thermal constraints

Coatings in general are made from either glass precursors through *in situ* reaction and melting or with ready-to-use glass frits. An aqueous slurry is prepared from these materials if the substrate is an unfired or a porous pottery. The slurry is deposited by immersion of the object or painting with a brush or spray dried. The slurry must have the right viscosity, thixotropy, *etc.*, which are optimized with specific additional ingredients such as clays, kaolin or polymers and glues. If the substrate is not porous, water is replaced with organic solvents/media and glues or similar

additives are incorporated. The coated items are then heated to form the glass coating and to develop a specific colour and/or gloss.

The coating thickness ranges from a few tenths of microns in *salted* stoneware to a few millimetres in *celadon* and *cloisonnés*. The coating must readily melt upon firing to yield a nice gloss and join smoothly with the substrate, which requires the precursor mixture to consist of a fine powder. Along with firing, grinding is the most energy intensive operation in the *Arts du Feu*, which might be why mechanized grinding techniques were developed only in the Middle-Ages with water mill energy. To get fine powders, ancient craftsmen thus relied instead on the firing of plants (ashes), shells and calcareous stone (chalk), bones (ashes), flint pebbles (silica) together with water washing to eliminate impurities. In this way they sometimes achieved directly the right composition (Fig. 1e) [6].

However, craftsmen have long known that composition is not the sole parameter that governs final quality [6-11]. For a given composition, the glaze can be matt or glossy, well coated (Fig. 3c) or crawled (Fig. 3d) depending on grinding time. The glaze ingredients used to be ground in a mortar or in a rotating barrel of water containing flint or quartz pebbles (now steel, alumina or zirconia balls depending on glaze composition). Upon firing, the reaction rate increases with the initial compaction of the deposit and it also depends on temperature, duration, heating rate, particle size, volatile content and on the reducing or oxidizing nature of the gas atmosphere. Because sintering is driven by atomic diffusion, longer heating times have similar effects as temperature increases or grain size decreases.

Controlling the contact angle between the melted coating and its substrate is mandatory to ensure complete wetting and also to keep the thickness constant. Bonding between the substrate and the coating is also very important. For metal substrates, a ground or under coat is generally needed to ensure adherence and accommodate the thermal expansion mismatch between upper coating and substrate [4]. Cobalt and nickel oxides were the best materials in this respect, followed by cupric, manganese and iron oxides. Glazes for decorative purpose were then applied on the ground coat.

Coatings widely differ in composition because of the thermal-expansion match that must be achieved with a great many different substrates during the firing and cooling operations. Two different techniques are distinguished in this respect. With the *Grand Feu* [Great Fire], for instance used to make porcelain, the coating and its substrate are simultaneously fired at temperatures ranging from 1200 to 1400°C. With *Petit Feu* [Small fire], Muffle fire or *mināi* (in Iran), lower temperatures of 600 - 1000°C suffice because the substrate has been separately fired once or twice at higher temperatures [10,11].

In practice, the thermal expansion coefficients of metals range from 100 to 220  $10^{-7} \text{ K}^{-1}$  (steel, 90-180; gold, 140; brass/bronze/copper 180-160; silver, 195; aluminium, 220  $10^{-7} \text{ K}^{-1}$ ). These coefficients are generally lower than 100  $10^{-7} \text{ K}^{-1}$  for ceramics (amorphous silica, 1 to 10; SiC, 35; mullite, 50; porcelain, 65; alumina, 75; zirconia, 105  $10^{-7} \text{ K}^{-1}$ ) and can even be negative for  $\beta$  spodumene/eucryptite (-10 to -5  $10^{-7} \text{ K}^{-1}$ , cf. Ch. 7.11). A further complexity results from the  $\alpha$ - $\beta$  phase transition of quartz, which causes a highly anomalous expansion near 565°C (Fig. 3) for quartz-rich raw materials. As for silicate glasses, their thermal expansion coefficient increases from 30 to 80  $10^{-7} \text{ K}^{-1}$  from borosilicates to lead-based materials, and decrease when  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$  or  $\text{ZnO}$  are substituted for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  [7]. Although thermal expansion of solids is a complex phenomenon determined at the atomic level by the number of bonds per unit volume and their anharmonicity, it has long been accounted empirically with coefficients first assigned to the constituting oxides by ceramist Hermann Seger (1839-1893). Optimised calculators are now available [12].

Another important property is tensile stress. As usual, it is much smaller on tension than on compression for silicate glasses. Because of its thinness, a coating should not be put under tension but gently compressed by the substrate. The slow expansion experienced by porous ceramics with time if exposed to humidity must also be accounted for. Upon cooling below the softening point, *i.e.*, the temperature at which the coating layer sticks on the substrate (Fig. 3) the contraction of the glass coating is monitored by the thermal expansion mismatch [4]. To result in a compressive stress, the thermal expansion of the glass should be lower than that of the substrate. On the contrary, a glaze crackles when the substrate expansion is too low (Fig. 4) whereas too high a compressive strength causes peeling.

The most common defects of coatings are volume bubbles, craters and pinholes induced by gas formation, generally from the body-interface reaction when glaze and body are fired together. However, small, micron-sized bubbles are specially developed in *celadon* (Fig. 3b) and opal glazes [9,10,13] for opacification or aesthetic effects.

### 3. Composition and microstructure

#### 3.1. Pottery glaze

The raw materials actually used are not oxides, but mineral substances such as stones, clays, feldspars, talc, quartz, flint or carbonates, the components to which craftsmen refer [4,6-9,14]. Because the compositions of these natural substances are highly variable, even within a given quarry, craftsmen mix raw materials from different places or, better, from different origins to average out differences and limit chemical fluctuations. When adjustments could not be made in the past in response to compositions changes, then the quality of the production was decreasing and the factory might even disappear.

Like materials scientists, archaeologists and art historians usually report glaze and enamel compositions in terms of oxides or elements as determined from chemical analysis (Ch. 5.1, [15]). Potters and enamellers put the emphasis instead on raw materials, which actually determine the actual firing process relevant to their batch (Table 1). They do it by following another procedure designed by Seger who distinguished acid [ $\text{SiO}_2$ ], amphoteric [ $\text{Al}_2\text{O}_3$ ] and basic [flux:  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{MgO}$ ] oxides [4,6,14]. The temperature, at which a liquid phase forms, a basic parameter for the reaction/bonding of the coating with the substrate, is then determined more by the particular raw materials used than by the mean chemical composition. Because the advancement of reactions (through atomic diffusion) depend on both temperature and time, Seger in addition designed reference cones made up of specific mixtures, which deforms and melts according given controlled firing conditions (temperature and heating rate) in the wide temperature interval 500 - 1520°C [12]. The interest of the procedure is apparent in Table 2 where firing temperatures range from ~600 (Cone 022) to ~1430°C (Cone 15).

Compounds such as lead oxide are highly volatile and diffuse rapidly in the substrate, however, in which cases compositions obtained from elemental analyses slightly differ from those of the precursors. Low-firing lead-free glazes maturing at 1050°C or less (Seger Cone #2) have from one to two parts of silica per part of the other ingredients. Higher-firing glazes melting at ~1250°C (Cone 10) have from three to five parts of silica per part of others. High-temperature fired porcelain glazes have ~10 parts or more of silica (Table 1).

These empirical rules are now complemented by fundamental insights derived from advances made through studies of structure-composition-property relationships (cf. section 2). Lowering of the melting temperatures by network-modifying cations such as Ca, Na, K, Li or Pb is well understood, as are the opposite polymerizing effects induced by the addition of Al. Raman spectroscopy (Ch. 2.2) is in particular used for rapid and non destructive analyses of chemical

bonds. The degree of polymerization of the coating is for instance derived from the ratio between the peak areas of  $\text{SiO}_4$  bending and stretching modes (Fig. 4), which markedly increases from fully depolymerised lead-rich glasses melted at about  $700^\circ\text{C}$  to 3-d connected silica-rich glazes melted at about  $1400^\circ\text{C}$  (Figs 4b-c) [14-18]. This direct relationship clearly illustrates how craftsmen have been unknowingly playing with the composition and degree of polymerisation of their coatings to achieve the required properties.

Finally, the duration of the complete heating and cooling cycle is of course another important parameter, which is largely determined by the thermal resistance efficiency of the insulating materials of the kilns. Many weeks were necessary for Chinese Dragon medieval kilns and a week was still common in 19<sup>th</sup> century. Until the 1960s, complete firing cycles were then down to several days. Thanks to the replacement of bricks with oxide-fibre felts in the 1980s, they have now been reduced to a few hours or even a few minutes for tile production.

### 3.2 Metal enamels

Bonding the glaze with the metal substrate involves a reaction with the oxidation layer formed at the metal surface. Copper and iron alloys have been first used because they develop easily on heating an adhesive oxide film. Coat and ground layers are added in modern enamels deposited on steel. Fluor addition promotes the reaction and the bonding (Table 3) [4].

### 3.3 Micro- and nano-structure

As determined by the starting materials and firing conditions, coatings display a wide variety of microstructures such as thin (Fig. 5a) and thick (Figs 5b,e,f) glaze layers or single (Figs 5a,c) and multi (Figs 5b,e,f) glaze layers. When examined in section, Iznik fritware represents a good example of a complex multilayered glaze that results from many firing sequences. The thinner glassy coatings are obtained by the *salting* technique whereby NaCl, lead oxide or plant ashes are poured (and volatilized) in the kiln, generally by the chimney when the kiln had reached its top temperature. The body can have a high (Fig. 5a) or a low porosity (Figs 5b, 5e and 5f), or no porosity at all (Figs 5c and 5d). Coarse quartz grains are obvious in Figs 5b, 5e and 5f bodies (composite bodies exhibit a better mechanical strength). Examples of underglaze (Fig. 5c) and overglaze (Fig. 5d) painted décor are given. Note in Fig. 5f, the very characteristic Iznik white quartz slip made of angular, crushed grains.

Because the glaze is almost liquid at the firing temperature it is rather difficult to keep a sharp separation between adjacent coloured areas. Different techniques have been used to limit this drawback, namely, direct painting on the green or porous body (underglaze décor), conservation of a line free of glaze precursor (often drawn with an oil-rich solution to avoid wetting by the glaze aqueous precursor, the *cuerda secca* technique), or addition of a highly refractory material such as either chromite [ $\text{FeCr}_2\text{O}_4$ ] or spinel [ $(\text{Mg,Fe})(\text{Al,Cr})_2\text{O}_4$ ] in Timuride and Iznik productions (Fig. 3e) or hematite in Mamluk glass-enameled artifacts (Figs 3c,d). Furthermore, the hematite matt layer can be used as a rough substrate to attach physically a thin gold foil [19]. Another notable property of non-stoichiometric crystals such as spinels and chromites is their ability to catch diffusing ions.

Actually many glazes contain micro or nanocrystalline secondary phases so that they are actually glass-ceramics (Ch. 7.11). Indeed, if the particle size is lower than  $\sim 1 \mu\text{m}$  the optical clearness is kept. This is the case of calcium-rich glaze in which wollastonite [ $\text{CaSiO}_3$ ] precipitates, common for Chinese and Vietnamese stonewares and *Celadons* [5,9,13], as well as for 18<sup>th</sup> century soft-paste European porcelains. The growth of the crystalline second phase yields a specific décor

largely experienced at the end of 19<sup>th</sup> century and in contemporary creation (Fig. 6d) [6]. Metal nanoparticles are another type of nanoprecipitates used as colouring agents as will be described in the next section (cf. Ch. 6.2).

#### 4. Coloration

The colour palettes on porcelain of the very beginning of 19<sup>th</sup> century of the Sèvres Manufacture (Figs. 6a) are nice illustrations of the hues that were then obtained [11,20]. Here, variations in hues were also determined by the different thicknesses of the enamel and small modifications of the composition [10,11,21]. As a general rule, the higher the firing temperature, the more difficult is the conservation of a large palette of shades. Because colouring agents were used in rather small quantities, elemental analyses either are not very efficient to identify them or involve very localized (destructive) methods [14,22,23]. Along with Diffuse Reflectance spectroscopy, Raman spectroscopy has proven to be the most efficient technique [2,13,15-22,24] especially when the frequency of the exciting laser is slightly higher than that of an electronic transition (the scattering intensities of bands coupled to this transition are then enhanced, and interferences with other bands reduced, which makes it possible to probe selectively chromophoric sites).

Glazes and enamel are colored in the same way as bulk glasses (Ch. 6.2). The simplest coloring agents are ions exhibiting electronic transitions in the visible range, such as transition metals ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ , etc.) or rare earths ( $\text{Pr}^{3+}$ ), which are incorporated into the glass network. Depending on the ion, contents in the 0.1 – 1 wt % range generally suffice for efficient coloration. Because the electronic energy levels depend on the structural environment of the ion, the actual hue varies with the chemical composition of the glass matrix (Ch. 6.2). The effect is especially strong for  $\text{Cu}^{2+}$ , which yields turquoise and green colors in alkali- (Fig. 3e) and lead-based (Fig. 6e) silicate glasses, respectively. The variety of colors achievable in this way is limited, however. Other routes have thus been developed, especially for thin layers in which pigments can be incorporated without dissolving in the glass matrix if they are refractory enough [4,6,9-13,20,24-28] (Tables 4-5). Good examples are spinels, corundum [ $\text{Al}_2\text{O}_3$ ], garnets [ $\text{X}_3\text{Y}_2(\text{SiO}_4)_3$ ] and zircon [ $\text{ZrSiO}_4$ ], whose very slow dissolution rates may actually cause real problems in glass making (Ch. 1.2).

A crystalline matrix can be specially prepared as a host for colouring ions to enhance colour and tune it more precisely. The pigment then is synthesized independently and incorporated into the batch. The reactivity of the pigment should be sufficiently weak to avoid its dissolution/modification in the molten glaze, however, which is why highly refractory phases with compact structures such as spinels, corundum, garnets and zircon are good matrices in this respect (Tables 4 & 5) [22].

Ancient pigments were usually silicate and lead-based compounds. The same cuprorivaite structure [ $\text{MCuSi}_4\text{O}_{10}$ ] has been used by Egyptian and Chinese craftsmen to prepare blue pigments, but with different alkaline earth cations, Ca and Ba, respectively. Natural pigments, such as Lapis lazuli, a semi-precious lazurite feldspar coloured through doping by  $\text{S}_x$  ions (Figs 3c), have been used at least since the Ptolemaic Dynasty to colour pottery glaze and enamels on glass objects [19]. Sixteen century later, Johann Friedrich Böttger (1682-1719) took advantages of the high colouring power of lapis lazuli to whiten the glaze of the first porcelains made in Europe in Saxony at the Meissen Factory (Fig. 2f) [29]). Alternatively, saturation in certain element leads to precipitation of phase(s) on cooling. Such a secondary phase precipitation can be tailored to opacify the glaze as done with cassiterite [ $\text{SnO}_2$ ], fluorite [ $\text{CaF}_2$ ], calcium antimonate [ $\text{Ca}_2\text{Sb}_2\text{O}_7$ ], lead arsenate [ $(\text{Pb,Ca})\text{AsO}_4$ ] and phosphates [2,10,11,13,22,28-31]. Unmixing (Ch. 5.2) is another type of phase separation that is tailored for special effects, for example for *aventurine*, *flammé*

(Fig. 6d) or *fur hare* (Fig. 6f) glazes, sometimes in combination with the formation of copper or iron metal particles, respectively [32].

A third way is to use metal nanoparticles (formerly called colloids) as pigments or as light-diffracting agents. Light is absorbed through its interaction with the electron gas formed at the metal/dielectric matrix interphase (Figs 1b, 2d, 6d, 6f & 7a). The strong peak observed in the UV-visible absorption curve (Fig. 7d) is due to the plasmon resonance of this electron gas and the broader features to interband electronic transitions [25]. Typically, particles of gold, copper, silver and iron yield ruby, red, yellow and grey colors, respectively. Glaze colored with colloidal gold has been spuriously named Cassius purple [22,25], after the chemist Andreas Cassius (1605-1673). The formation of metal nanoparticles requires controlling redox equilibria within the glass. Burning wet wood to produce hydrogen, which diffuses rapidly in the glass network, was a simple way to do it. Another, indirect way was fast diffusion of multivalent ions reduced at the glaze/enamel surface ( $\text{Fe}^{3+/2+}$ ,  $\text{Sn}^{4+/2+}$ ,  $\text{Sb}^{5+/3+}$ ,  $\text{Eu}^{3+/+}$ ) [25,26,33]. Good examples demonstrating how aesthetic combinations of red and turquoise colours can be achieved through the different oxidation states of Cu ions obtained in kilns (Fig. 6d) [30-34] are *Jun*, *flammé* and Art Nouveau pottery.

A fourth method of colouration is based not on light absorption but on diffraction. The technique is extensively found in Nature (opals, mother of pearl, butterfly wings, beetles, cephalopods or tridacna). The colour arises from constructive/destructive interferences formed by the quasi-periodic organisation at the layer nano-level. This surface effect is called *lustre* [French *lustre*, from the Latin *lustrare*, to illuminate] (Figs 1b, 6f, 7a). It dates back to the Islamic Abbasid dynasty (9<sup>th</sup> century) [25,34] during which the alternation of layers rich and poor in metal particulates forming the lustre was achieved by controlled sequences of oxidising/reducing atmospheres by deposition of a mixture of Ag/Cu salt, clays, ocre or organic compounds (vinegar, grape must, etc.) on the already glazed surface of the pottery. On heating (~600°C) silver and copper ions diffuse in the glaze and form metal nanoparticle-rich layers under the action of the reducing atmosphere and redox equilibria. Then the precursor mixture is eliminated by washing and the lustre décor revealed [25,33]. .

*Gilding* or *silvering* are yet other methods to coat a glass artifact with a coloured metal layer of Au (Figs 1a, 2a, 2b, 2d, 3c (traces) and 3f) or of silver (Ag) [35]. Brass and mercury alloys are also used [36]. The metal layer can be bonded chemically or physically thanks to a rough surface. Different techniques initiated during the Renaissance are possible (addition of  $\text{Bi}_2\text{O}_3$ , resinates, etc.). Finally, one obtains a white colour by dispersing a second phase with a particle size comparable to that of the wavelength of visible light and a refractive index differing from that of the glass matrix. Examples are air bubbles, quartz, cassiterite (Figs 1b, 1c, 3e & 6c), fluorine (Fig. 1d), calcium phosphate, lead arsenate, zircon or zirconia.

## 5. Enamels

### 5.1. On metals

Early craftsmen first solved the fluidity problem by the *champlevé* technique [from the French *champ*, the background of the shield, in heraldry, and *levé*, removed], whereby the metal substrate was carved to form rifts that retained the molten glass in the intended decorative pattern during the firing. More intricate decors were achieved in the 2<sup>nd</sup> century B.C. through the replacement of the carved regions with thin walls made up of metal foils called *cloisons* [thin walls, in French], a thin metal strip perpendicular to the substrate delineating the different coloured areas and forms depicted, Fig. 1d). The first were made by Celts on various metals and in Byzantium, mainly on gold. The *champlevé* and *cloisonné* productions on gold or silver substrates flourished throughout



the Byzantine Empire and in neighbouring Kiev and Georgia Kingdoms, as well as in the Western Carolingian Kingdom and Otton's Roman Empire (7<sup>th</sup> – 11<sup>th</sup> c.) [2,31]. In the 12<sup>th</sup> and 13<sup>th</sup> centuries, Limoges (France) and Silos (Spain) became large production centres in relation to the Muslim culture of *al-Andalus*. Silver substrates were then used in Italy from the 14<sup>th</sup> century onward.

A medieval Chinese report calls enameled work *production from the Devil countries* [*guiguo yao*], *i.e.*, the West [31]. When the production of *cloisonné* enameled objects nonetheless eventually developed in China from the 16<sup>th</sup> century (Fig. 1c), the technique had almost disappeared in Europe. The reason had been the emergence toward the end of the 15<sup>th</sup> century [2] at Limoges of a *painted enamelling* (Fig. 2 a-b), an elaborate technique in use at the same time in Burgundy and the Netherlands as well as in other parts of France and Europe. Painted *Limoges* enamels consist of multilayer paintings deposited on a copper support through successive firings of different compositions (Figs 2a & 2b). The back side is also enameled and the artifact polished after firing. This technique called *falang* [Frank, in Chinese] was more sophisticated than earlier ones such as *cloisonné* with which the same glass matrix can be used for different colours. Like the potters of the *majolica* ceramics, craftsmen depicted very complex motives from episodes of antique legends or biblical themes. Around 1530–1540, yet another new kind of enamel employed a limited number of colours, mainly black and white [hence the name *grisaille*, greyness], to enhance the visual effects in the flesh areas of the human figures depicted. During the 17<sup>th</sup> century, the quality of enamels began to decrease until a remarkable revival took place in the 19<sup>th</sup> century: the workshops not only produced modern *Limoges School* pieces, but also replicas of Renaissance enamels which were also often being sold as originals (Fig. 2b) [2].

## 5.2. On glass

Even though high-quality glass artifacts have been produced in large quantities ever since the beginning of Roman times (Ch. 10.3, 10.4, [19,21,35]) dichroic/lustre and enameled glass are very rarely reported in the ancient literature [10] or represented in Museum collections [19,21,35]. Major examples of preserved enameled glass objects are remains of the Afghan Begram Treasure (1<sup>st</sup> century AD; Musée Guimet, Paris), the fragments of the Lübsow cup found in Poland (2<sup>nd</sup> century AD) or the Cohn Beaker & Hans Cohn Collection, which is supposed to have been found in Egypt [19,21]. The evidence becomes infrequent from these early periods until the Islamic and Venetian productions of the 13<sup>th</sup> century. The few remaining pieces representative of the whole Byzantine period are a group of gilded and occasionally enameled vessels from Corinth and Paphos together with a series of sparse objects, all dated between the 10<sup>th</sup> and the 11<sup>th</sup> century, and the famous San Marco Bowl also dated to the 10<sup>th</sup>/11<sup>th</sup> century and probably brought back to Venice after the sack of Constantinople in 1204 by the Crusaders.

With the enameling and gilding technologies developed at the Norman/Swabian Court of Frederik II (recent excavation at Melfi Castle, Southern Italy, 13<sup>th</sup> century) and in Syria and Egypt [19] during the Ayyubid and Mamluk periods, pieces were then exported all over the ancient World from Europe to China. Mamluk Mosque lamps, mostly hanging, are among the most magnificent evidence of the technical virtuosity of those glassmakers. The use of lapis lazuli, as ceramic or glass pigment has long been denied by scholars. But the presence of lapis lazuli powder, sometimes mixed with cobalt ore, has recently been demonstrated in pottery glazes and glass enamels of the 14<sup>th</sup> century [19]. Furthermore, a more ancient use of lapis lazuli has been documented down to the 1<sup>st</sup> century or even before with the glass treasure discovered in Afghanistan at Begrâm or Ptolemaic glazed pottery from Pompeii [19].

The development of chemistry at the end of the 19<sup>th</sup> century offered a variety of routes to colour a glass matrix and enamels. In France Philippe-Joseph Brocard (1831-1896) and Emile Gallé (1846-

1904) were very innovative craftsmen famous for their masterpieces (Fig. 2c) [36]. Brocard's approach, the mixing of a variety of colouring agents, may have been related to his self-teaching of glassmaking, as opposed to the more traditional technology so that his expertise in various fine arts was representative of the 19<sup>th</sup> century technical innovation spirit. On the other hand, Gallé took advantage of his traditional glassmaking expertise to create new forms, with innovative shapes and colour associations, contributing to the novelty of Art Nouveau aesthetics. The most striking innovations at the turn of 19<sup>th</sup> / 20<sup>th</sup> century was the use of  $\text{CdS}_{1-x-y}\text{Se}_x\text{Zn}_y$  semiconductor nanoprecipitates to prepare vivid red to yellow and of  $\text{UO}^{2+}$  ions for yellow glaze [4,10,24].

## 6. Glazes

As produced in the Middle East from about 2000 B.C., glazes were fired at about 900-1000 °C and coloured or opacified with lead antimonate yellow [ $\text{Pb}_2\text{Sb}_2\text{O}_7$ ] and calcium antimonate white [1,22,31]. More elaborate techniques were then designed, for instance in Egypt by potters of the 22<sup>th</sup> Egyptian Dynasty (945-715) who took advantage of an efflorescence phenomenon on the sample surface during the drying process to form an *in situ* layer of glass/colouring agent precursor [1]. Another notable feature was the real mass production achieved not only by Roman glassmakers (Ch. 10.3) but also potters with *sigillata* [stamped earth] for instance exported in the first century as far as Syria, Egypt and the Black sea from the Graufesenque workshops in Central France. The surface layer was intermediate between a glaze and a slip and coloured with hematite [ $\text{Fe}_2\text{O}_3$ ], hercynite spinel [ $\text{FeAl}_2\text{O}_4$ ] or pseudobrookite [ $(\text{Fe}^{3+},\text{Fe}^{2+})_2(\text{Ti},\text{Fe}^{2+})\text{O}_5$ ] [23].

In the Far East, Chinese Eastern Han to Sui potters (2<sup>nd</sup> B.C. –7<sup>th</sup> c.) really initiated high-temperature firing technology thanks the building of advanced kiln. Temperatures higher than 1300°C were achieved as early as in the 3<sup>rd</sup> century for the feldspathic Yue stoneware [5,9]. The first glazes obtained using plant ashes were used as décor (Fig.1e) in a fashion that looks very modern from an aesthetic point of view.

White porcelains then appeared during the Sui and Tang Dynasties (7<sup>th</sup>–8<sup>th</sup> c.) [5,9]. At the same period Islamic potters found how, when combined with low-temperature firing, the (5<sup>th</sup> c.) Roman glassmaking technique of opacification by cassiterite [ $\text{SnO}_2$ ], could compete with high-temperature fired porcelain to produce artifacts with complex depictions [33,34-37]. This innovation resulted from the imitation of the three-color Tang Chinese porcelain wares with lead-rich blue and green glaze dots deposited on a faience/*terra cotta* body covered with an alkaline glaze [37]: the chemical reaction between the two glazes caused white cassiterite to precipitate. The use of cassiterite opacifier spread around the Mediterranean Sea with the expansion of the Islamic World, namely, in *Ifriqaya* (7<sup>th</sup> c.), *al Andalus* (8<sup>th</sup> c.), Sicily (9<sup>th</sup> c.) and then to Italy (*majolica*, 13<sup>th</sup> c.) and France (15<sup>th</sup>–16<sup>th</sup> c.) [27,28,33,37]. A composition shift took place from calcium-rich (ash-based) glazes during the 10<sup>th</sup> century Five Dynasties to potassium-rich (feldspar-based) Song glazes (12<sup>th</sup> c.). Interestingly, a similar evolution took place with delay in Vietnam from the Ly to the Tran dynasties between the 11<sup>th</sup> and 14<sup>th</sup> centuries [13].

Blue-and-white Yuan porcelains were first prepared with cobalt pigments that could come from Iran (or Saxony, Europe) through the Silk Road thanks to the *Pax Mongolica*. Local cobalt ores were then used but these Asian sources had high Mn and Fe contents. Especially when their fuel was coal, Chinese and Vietnamese potters empirically controlled the firing atmosphere of their kilns to obtain the strongly reducing conditions required to produce the blue colour desired [9,13]. As optimized in China, the blue decor was drawn on the body (underglaze décor, Fig. 8c) or on the glaze (Fig. 8d). The first technique was optimised in China while Vietnamese potters preferred overglaze décor.

Attempts to imitate the blue-and-white Chinese porcelain were first made by Islamic potters. Top-quality pieces were made in Anatolia, for instance at Iznik [the ancient Nikaia] where manufacture(s) developed fritwares between around 1450 and 1620 (Figs 5e-f, 6c) [36]. In Italy the Duke of Medici's porcelain (Fig. 2e), a material intermediate between fritware and hard-paste China, was produced from about 1575 to 1587 with the help of a Master coming from the Levant [38]. At the end of the 17<sup>th</sup> century, manufactures of soft-paste porcelain (silica-rich body made a quartz grain cemented with a glass, a sort of fritware) appeared in France (Rouen, Saint-Cloud, Paris, Chantilly, Vincennes, Tournai, Mennecey) before factories of hard-paste porcelain (Fig. 1 a-b) developed in the whole of Europe (Meissen, Strasbourg, Vienna or Saint-Petersburg) [20,38,39]. Also called China, hard-paste porcelain is made from kaolin and feldspar. It is an alumina-rich body transformed into acicular mullite crystal frame (~30 % in volume) soaked with a glassy matrix. The major difficulties were to build kilns reaching 1450°C and to maintain such high temperatures for a few days. Consequently the first European tentative at Dresden to fire hard-paste porcelain relied on a solar beam and lenses! Iznik potters first used a cassiterite opacifier in a lead-based glaze but rapidly replaced this technique by a slip made of crushed quartz grains covered by a transparent glaze (Fig. 6c and Figs 5e-f). These grains act as light reflectors that give rise to the powerful colours of Iznik décors. The very efficient control of Ottoman authorities, the *Nakashame*, led to an exceptional quality of production for about a century [40]. Later, Kütahya manufactures (Fig. 1c) maintained the creativity of Ottoman glazed fritwares. Ottoman potters produced multilayer glazed artifacts requiring multi firing cycles (Fig. 5e-f). The soft-paste porcelain route can actually be considered as an evolution of the Iznik fritware technology since the body consists of quartz grains cemented with the frit. When kaolin was eventually discovered in Europe in the 18<sup>th</sup> century, its availability allowed for the preparation of hard-paste alumina-rich porcelain. Its high refractoriness led to design new glaze compositions. A revolution thus took place after 1750 with the development of faience and porcelain factories in Europe [20,22].

Elegant white Song porcelains were largely exported, including in Japan. Throughout the 13<sup>th</sup> to 16<sup>th</sup> centuries, however, some Japanese scholars began to prefer Chinese and Vietnamese stonewares. Their simplicity and imperfections were more highly praised than the highly aesthetic Song style (10<sup>th</sup>-13<sup>th</sup> c.), as a result of the *wabi-sabi* Movement and the development of the Tea Ceremony [41]. During the Momoyama period (1573-1615), local potters, in particular those of the Raku Family, already very active, developed a highly original style. Unpredictable kiln effects (*i.e.*, defects!) were desired for these “accidentally lovely” works used as flower vases and utensils for the Tea Ceremony [41]. The discovery of this production at the first *Expositions Universelles* [World fairs] led to the *Japonism* and *Craft* aesthetic movements, which have largely inspired a large part of the contemporary pottery production. These have even been at the roots of the renewal of the *cloisonné* enamel technique in Europe at the end of the 19<sup>th</sup> century.

## 7. Perspectives

The second half of the 20th century has seen extensive merging of companies in the ceramics and glass industries. Enamels formerly made in traditional manufacturing processes are now produced by a limited number of companies, which has led to a standardization of technologies and products. Only rare creative potters made again their enamels themselves. The best control of the heating (kiln) and insulation processes have also strongly modified the procedures whereas wood firing has almost disappeared. Some coloring elements have become either too expensive or toxic, in which case they are now prohibited (*e.g.*,  $\text{UO}^{2+}$  yellow, CdS-CdSe red to yellow). As another example, the European Union plans to prohibit the use of lead, even if its encapsulation in silicate networks guarantees the absence of a reaction. Searches are being conducted to replace lead with other fluxes such as boron, bismuth although it remains to establish whether the new compounds

obtained are actually less prone to release undesirable elements. On the other hand, sol-gel routes (Ch. 8.2) allow coatings to be processed at much lower temperature [42] than the usual ceramic and glass routes, which has led to innovative products such as enameled aluminum kitchen stoves.

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Table 1. Modern porcelain glaze compositions expressed in terms of either oxide or raw materials (wt %, after [43]).

Raw materials	Oxide	NG6 Glaze	NG33 Glaze
	SiO <sub>2</sub>	63.16	73.87
	Al <sub>2</sub> O <sub>3</sub>	17.87	14.31
	CaO	11.46	4.95
	K <sub>2</sub> O	5.72	4.85
	Na <sub>2</sub> O	1.37	1.16
	Fe <sub>2</sub> O <sub>3</sub>	0.19	0.14
	TiO <sub>2</sub>	0.05	0.03
	MgO	0.19	0.69
Standard kaolin (ECC) <sup>a</sup>		8.70	7.85
Calcined kaolin (Dorkamul) <sup>b</sup>		13.16	8.75
Quartz (Norquartz 45) <sup>c</sup>		6.89	33.35
Feldspar (Norflux 45) <sup>c</sup>		45.67	38.45
Wollastonite FW325 (Partek) <sup>d</sup>		25.58	8.90
Dolomite (Microdol 1) <sup>e</sup>		-	2.70
Firing temperature (°C)		1340	1400

<sup>a</sup> English China Clay (St. Austell, UK)  
<sup>b</sup> Dorfner (Hischau, Germany).  
<sup>c</sup> North cape Minerals (Stjernoy, Norway);  
<sup>d</sup> Partek (Helsinki, Finland)  
<sup>e</sup> Norwegian talc (Bergen, Norway)

Table 2. Modern glaze compositions expressed with Seger formula (after [4])

Glaze type	Cone	Acid	Amphoteric	Basic (Flux)			CaO	SrO	Li <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O	ZnO	B <sub>2</sub> O <sub>3</sub>	PbO (P <sub>2</sub> O <sub>5</sub> )
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub> (SnO <sub>2</sub> )	Fe <sub>2</sub> O <sub>3</sub>	MgO								
Silica-rich	15	0.8333	0.0833				0.0583			0.025				
	7	0.7143	0.0816			0.0204	0.1429			0.0408				
Alkali-rich	11	0.6593	0.1209				0.1319			0.022	0.022	0.044		
	4	0.6275	0.0784				0.098			0.049	0.049		0.098	
Tableware	4	0.638	0.0673	0.0104			0.0878	0.0899		0.0251	.0063		0.0752	
	4	0.6679	0.081			0.0223	0.0638	0.0911	0.0061	0.0152	0.0607		0.0506	
Majolica	1	0.6688	0.0495			0.0274		0.0547		0.0223	0.0983		.079	
Low expansion	10	0.6477	0.0646	0.1062		0.0751	0.0262			0.0215	0.0138	.0185	0.0277	
	1	0.5805	0.161	0					0.1973	0.0295			0.0204	
Lead-based	4	0.6281	0.0753				0.0684			0.0165	0.0418	0.076	0.0606	0.076
	010 <022	0.6599	0.0719											0.2682
Aventurine Crackle	4	0.5795	0.0886		0.0453	0.0407	0.0724			0.0277	0.0954	0.0524		0.5211
	06	0.5461	0.0848				0.0039			0.0519	0.1426	0.0083	0.1617	
Raku	06	0.587	0.0723	0.0192		0.0023	0.0034			0.0362	0.1170	0.0056	0.1566	
Celadon Chun/Red Ash	6	0.7422	0.0918			0.0029	0.0065	0.1206			0.0345	0.0011		(0.0005)
	8	0.7718	0.0619			0.0064	0.0237	0.100		0.02604	0.0072			(0.0022)
	4	0.316	0.0673			0.0062	0.0479	0.2561		.030	0.1874		0.0827	(0.0053)
	8	0.4611	0.0996			0.0058	0.0269	0.1740		0.0346	0.1705			(0.0041)
		Si	Al	Zr/Sn	Fe	Mg	Ca	Sr	Li	K	Na	Zn	B	Pb

Table 3. Representative metal enamel composition (after [4])

Enamel type	Tp °C	Acid	Amphoteric	Basic (Flux)										
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub> (TiO <sub>2</sub> )	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	NiO (CoO) (0.0045)	Li <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O	ZnO (BaO) (0.0186)	B <sub>2</sub> O <sub>3</sub>	F (P <sub>2</sub> O <sub>5</sub> )
Ground coat	805	0.4987	0.0382			0.0013	0.0718	0.0101 (0.0045)	0.0109	0.0103	0.1357	(0.0186)	0.1299	0.0650 (0.0016)
Cover coat	770	0.3905	0.0114	0.010 (0.141)		0.0019			0.0160	0.0438	0.0828		0.1205	0.1763 (0.0055)

Table 4. Pigments used in the 20<sup>th</sup>-21<sup>th</sup> centuries

Pigments	Crystal structure	Colour
Co(Al,Sn) <sub>2</sub> O <sub>4</sub>	Spinel	Blue
CoSiO <sub>4</sub>	Olivine	Blue
CoAl <sub>x</sub> Cr <sub>2-x</sub> O <sub>4</sub>	Spinel	Blue-green
(Zn,Fe)(Fe,Cr) <sub>2</sub> O <sub>4</sub>	Spinel	Black
CuCr <sub>2</sub> O <sub>4</sub>	Spinel	Black
Zn(Al,Cr) <sub>2</sub> O <sub>4</sub>	Spinel	Pink
3CaO Cr <sub>2</sub> O <sub>3</sub> 3 SiO <sub>2</sub>	Sphene	Victoria Green
Pb <sub>2</sub> Sb <sub>2-x</sub> (Sn,Si,Fe..)O <sub>7</sub>	Pyrochlore	Naples yellow
ZrSiO <sub>4</sub> :V	Zircon	Blue
ZrSiO <sub>4</sub> :Pr	Zircon	Yellow
ZrSiO <sub>4</sub> :Fe	Zircon	Pink
ZrO <sub>2</sub> :V	Zircon baddeleyite	
SnO <sub>2</sub> :V	cassiterite	yellow
Al <sub>2</sub> O <sub>3</sub> :Cr	corundum	Ruby
(Al,Cr) <sub>2</sub> O <sub>3</sub>	corundum	Red
Cr <sub>2</sub> O <sub>3</sub>	corundum	green
Fe <sub>2-x</sub> (Al,Ti,Mn) <sub>x</sub> O <sub>3</sub>	Hematite (corundum)	Red
Fe <sub>2-x</sub> Al <sub>x</sub> Ti <sub>x</sub> O <sub>3</sub>	Hercynite (spinel)	Red
(Co,Ni)O	Periclase	Gray
(Co,Zn) <sub>2</sub> SiO <sub>4</sub>	Phenacite	Blue
(Ti,Ni,Nb,Cr,Sb)O <sub>2</sub>	Rutile-Cassiterite	Brown
(Sn,V)O <sub>2</sub>	Rutile-Cassiterite	yellow
ZrSiO <sub>4</sub>	Zircon	White
ZrO <sub>2</sub>	Zircon	White
CdS <sub>1-x</sub> Se <sub>x</sub>	Wurtzite	Yellow (S) to red (Se)



Table 5. Main ancient pigments

Pigments	Structure	Composition	Colour	Date
Lazurite (Lapis Lazuli)	Feldspathoid	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\cdot\text{S}_x$	ultramarine	Roman
Ultramarine	zeolithe	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\cdot\text{S}_x$	ultramarine	> ~1830
Co-olivine	olivine	$\text{Co}_2\text{SiO}_4$	blue	>1500
Sèvres blue	Spinel	$\text{CoAl}_2\text{O}_4$	blue	>18 <sup>th</sup>
Egyptian Blue	amorphous	$\text{CaCuSi}_4\text{O}_{10}$	blue	3000 BC
Egyptian Green		“	green	3000 BC
Han blue		$\text{BaCuSi}_4\text{O}_{10}$	blue	500 BC
Han violet		$\text{BaCuSi}_2\text{O}_{16}$	violet	~200 BC
Smalt	amorphous	Co in glass		> 1300
Bone white		$\text{Ca}_2\text{PO}_4$	white	Roman
Rutile	Rutile	$\text{TiO}_2$	white	>20 <sup>th</sup>
Quartz	quartz	$\text{SiO}_2$	white	>5 <sup>th</sup>
Tin oxide	Cassiterite	$\text{SnO}_2$	white	>5 <sup>th</sup>
Wollastonite		$\text{Ca}_3\text{Si}_3\text{O}_9$	white	>18 <sup>th</sup>
Arsenate		$(\text{Pb,Ca})\text{AsO}_4$	white	>16 <sup>th</sup>
Uranyl yellow		$\text{UO}^{2+}$ in (lead)glass	yellow	>19 <sup>th</sup>
Cadmium sulphide-selenide	Wurtzite	$\text{CdS}_{1-x}\text{Se}_x$	Yellow to red	>20 <sup>th</sup>
Naples Yellow Type 1	Pyrochlore	$\text{PbSn}_{1-x}\text{M}_x\text{O}_4$	Yellow	Roman
Naples Yellow Type 2		$\text{PbSn}_{1-x}\text{Si}_x\text{O}_4$	Yellow	Roman
Naples Yellow pyrochlore		$\text{PbSb}_{2-x}\text{M}_x\text{O}_7$	Yellow	Antiquity
Zinc Yellow	Spinel	$\text{ZnCrO}_4$	Yellow	>19 <sup>th</sup>
Mussif Gold		$\text{SnS}_2$	Gilding	>13 <sup>th</sup>
Hercynite	Spinel	$\text{Fe}_2\text{-}_x(\text{Al,Ti,Mn})_x\text{O}_3$	Orange	Roman
Hematite	Corundum	$\text{Fe}_2\text{-}_x(\text{Al,Ti,Mn})_x\text{O}_3$	Red	Roman
pseudobrookite	brookite	$\text{Fe}_{2-x}(\text{Al,Ti})_x\text{O}_5$	Red	Roman
gold	Metal	Au	Red	15 <sup>th</sup>
	nanoparticle		purple	
Copper	“	Cu	red	<5 <sup>th</sup> B.C.
Silver	“	Ag	yellow	12 <sup>th</sup>

Table 6. Mean compositions of some enamels on metal substrates ([after 2]).

Type	Origin	Date century	SiO <sub>2</sub>	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	PbO
Painted	Limoges, Burgundy, Venice Limoges	15 <sup>th</sup>	39-70	2.5-5	3-16	7-16	0-22.4
		16 <sup>th</sup>	42-55	5-6.5	1-5.5	8-8.5	23-35
		16 <sup>th</sup>	55-73	3	5-8	5-10	-
		16 <sup>th</sup> -17 <sup>th</sup>	62	4.5	4.5	-	2.5
		17 <sup>th</sup> -18 <sup>th</sup>	61	3.1	5.5	-	13.8
		19 <sup>th</sup>	48	1.7	8	-	32.4
		16 <sup>th</sup> -18 <sup>th</sup>	53	6.4	5.2	-	27.2
Cloisonné	Paris & Spain China	14 <sup>th</sup>	60	2-8	4-15	9-15	0-2
		16 <sup>th</sup>	40-45	5-6	8-10	0.5-15	30-37
		17 <sup>th</sup>	45-60	5-15	5-10	0.5-10.5	15-22

Table 7. Mean compositions of some glaze layers on terra cotta, stoneware, hard- and soft-paste porcelain bodies (after [5,9,11,13]).

Type	Origin / century	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	PbO	P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	B <sub>2</sub> O <sub>3</sub> (ZnO)
Terra cotta	Anatolia	27.1	3.8	2.1			62.8		3.02			
Celadon	Anatolia	40.4	10	1.8	1		42.9		2.9		1	
	Five Dynasties	59.4	16	16	3.4	0.3			1.8	0.4	2	
	Northern Song	63.2	16.8	13	3.3	0.6			1.4	0.2	1.1	
	Southern Song	68.6	14.3	10.4	5	0.1			0.7		0.4	
	Yuan	67.4	16.7	6.8	5.5	1.1			1.5	0.2	0.6	
	Yue 10 <sup>th</sup>	58	12	20	1.5	0.8		1.5	2.2	0.8	2	
	Hop Lê	78.6	15.5	1.5	1.8				1.2	0.7		
	Koryo	73	17	0.5	2.6	0.8			2.5	0.9	0.5	
	Southern Song 10 <sup>th</sup> -13 <sup>th</sup> (Longquan)	67	14.5	10	5	0.5	-	0.6	0.5	0.1	1	
	Northern Song 12 <sup>th</sup> (Jun)	71	10	10	3	0.5	-	0.5	<2	0.4	1.5	
Hard-paste	Northern Song 10 <sup>th</sup> -13 <sup>th</sup> (Ding)	72	17	3	2	0.5	-	-0.2	0.5	0.2	2.3	
	Vietnam 15 <sup>th</sup>	64	17	7	2.5	0.3	-		1.2	0.8	0.5	
	Yuan (b&w)	74.3	19.7		2.3	2.3		0.3	1			
	Böttger Meissen early 18 <sup>th</sup>	61	33	4.8	0.1	0.2						
	Meissen 18 <sup>th</sup>	59	35	0.3	4	0.8			0.3	0.1		
	Terre de Lorraine 20 <sup>th</sup>	64	30	1.2	2.3	2.2					0.2	
	St-Cloud	66.2	8.3	6.95	0.5	6.5			0.2	0.01	0.8	1.75 (2.2)
		76	1.75	12.6	3.1	2.9	0.1		0.7	0.1	1.4	
	Vincennes	72.9	2.1	15.7	4.3	2.7	0.2		0.3	0.1	0.8	
	Sèvres	74.2	2.2	15.7	0.3	2.1	0.2		0.3	0.1	0.8	
Soft-Paste	Terre de Lorraine	56.4	21.4	16.1	2.5	0.9		0.6	0.8	0.5	0.4	
	Bow (Bone ash)	45.6	8.7	23.6	1.1	0.8		18.6	0.6	0.5	0.6	
	Worcester (soapstone)	74.1	3.8	1.9	2.8	1	4.9			0.3	10.8	
	Longton Hall	77.2	2.9	8.8	3.7	0.8	6.3					
	Buon Retiro	79.8	4.65	0.2	2.1	0.5			0.4		12.4	

## Figure Captions

Fig. 1. A variety of glass coatings. (a) enameled Venetian chalice (circa 1480-1500); (b) glazed Ottoman Kütahya bowl (end of 17<sup>th</sup> c.); (c) Hispano-Moresque Lustre pottery (15<sup>th</sup> c.); (d) Chinese cloisonné (16<sup>th</sup> c.); (e) Han Viet pottery glazed with ashes ( before 6<sup>th</sup> c.); (f) Raku tea bowl (20<sup>th</sup> c.) voluntarily broken and restored with the golden lacquer technique (courtesy Andoche Praudel, potter); Photos Ph. Colomaban.



**Fig. 2.** Limoges enamels. (a) Plaque depicting Jesus before Ponce Pilate tentatively assigned to Penicaud (16<sup>th</sup>/17<sup>th</sup> c., UCAD coll., partially restored); (b) Plaque depicting King Henry IV (initial 17<sup>th</sup> c. dating, actually a 19<sup>th</sup> c. fake; UCAD PE1640); (c) Gallé enameled glass (UCAD Coll); (d) Sceaux porcelain ewer decorated with Cassius Purple enamel (MNC Sèvres Coll.); (e) Medici porcelain plate (16<sup>th</sup> c., MNC Sèvres Coll.); (f) Rhinoceros from Pilnitz garden (J.F. Böttger, Meissen, early 18<sup>th</sup> c., MNC Sèvres Coll.), Photos Ph. Colomban.



Fig. 3. Firing defects on glazes and enamels. (a) Celadon crackled glaze (19<sup>th</sup> c., Qing Dynasty); (b) High-quality Mamluk enameled glass bottle exhibiting a high-quality glossy enamel (14<sup>th</sup> c.); (c) Mamluk enameled mosque lamp where the glaze has failed to adhere to or wet the body on firing (crawling); (d) *Cuerda seca*-like technique : a line hinders the glaze to go out of the defined area (15<sup>th</sup> c., Ottoman Empire) [6]; (e) micro-crazed red glaze of a gilded Meissen Bottger' stoneware; Photos Ph. Colomban.

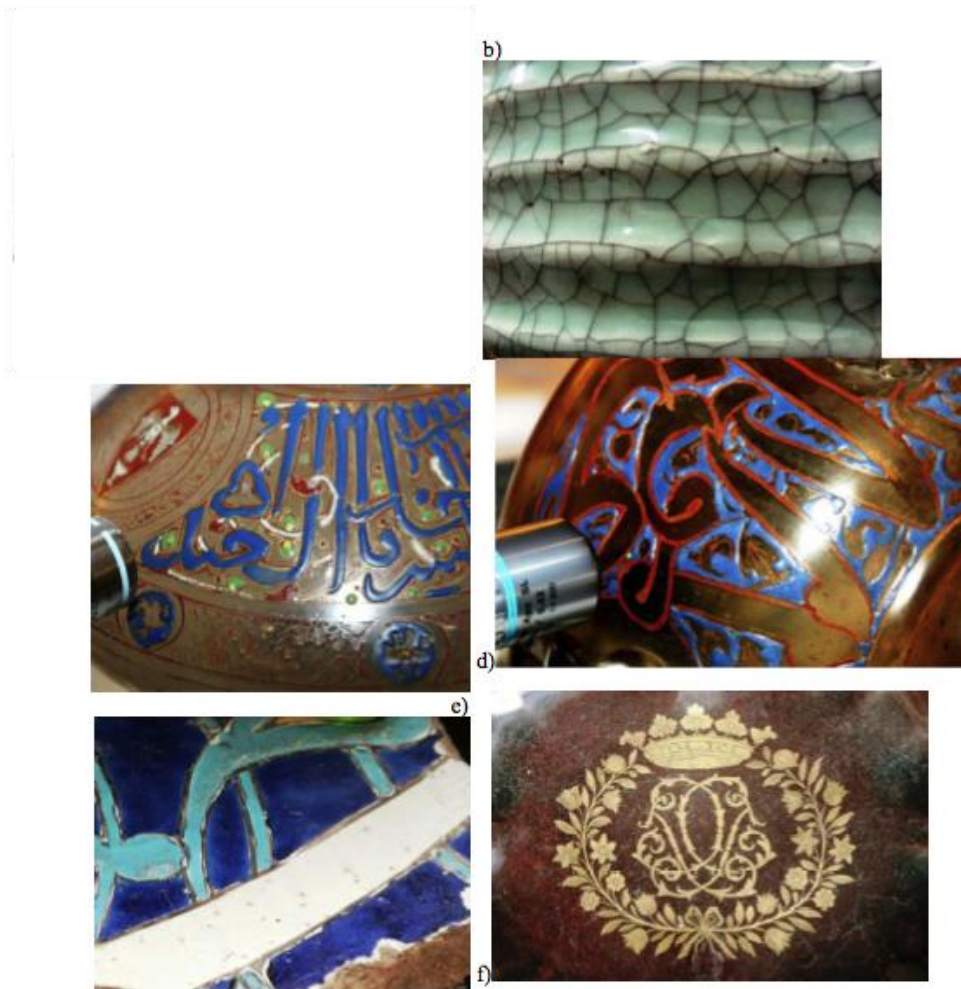


Fig. 4. Control of the glaze quality: comparison between the thermal expansion of a quartz-rich ceramic body (solid line,  $\alpha - \beta$  phase transition) and a glaze (dashed line;  $T_g$ : glass transition temperature; s.p.: softening point).

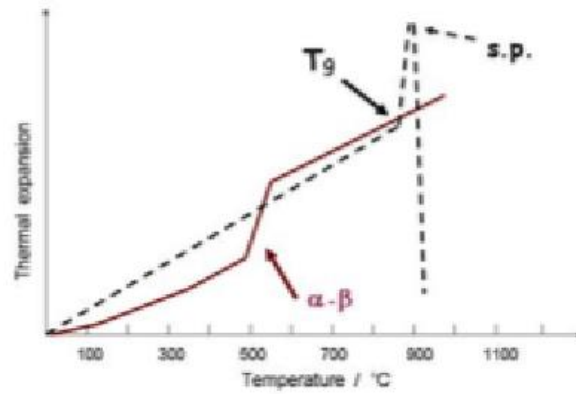


Fig. 5. Structure and polymerization of silicate glasses. (a) Sketch of the network made of more or less connected  $\text{SiO}_4$  tetrahedron with fluxing ions in between; (b) Typical Raman spectrum showing the stretching and bending bands pertaining to the different types of tetrahedra (from  $Q^0$  to fully connected  $Q^4$ ); boson peak subtracted [19,20]; (c) and (d): polymerization index (*i.e.*, ratio of the bending and stretching band areas) for crystalline and amorphous silicates, respectively, after [16-18]; main fluxes and other oxides indicated.

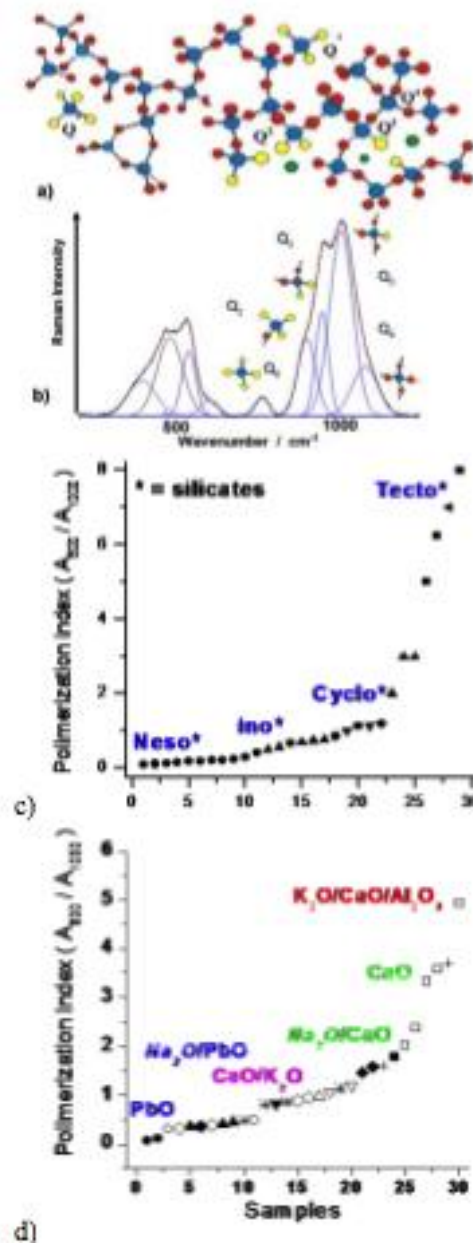




Fig. 6. Optical micrographs of sliced sections of glazed potteries. (a) Lead-rich glaze on terra cotta (14<sup>th</sup> c., Oman Sultanate); (b) Ottoman lead-alkaline glaze on clay-rich tile tempered with quartz grains (15<sup>th</sup> c.); (c) Chinese glazed stoneware with an under-glaze dark blue décor (15<sup>th</sup> c.); (d) Chinese blue over-glaze décor on porcelain (17<sup>th</sup> c.); (e) Ottoman Iznik glazed tile, with a 3mm-thick white quartz grain-rich slip over the body (fritware) and the multilayer glazed blue and red overglaze (16<sup>th</sup> c.); (e) detail; Photos Ph.

Colomban except e and f, courtesy G. Simsek.

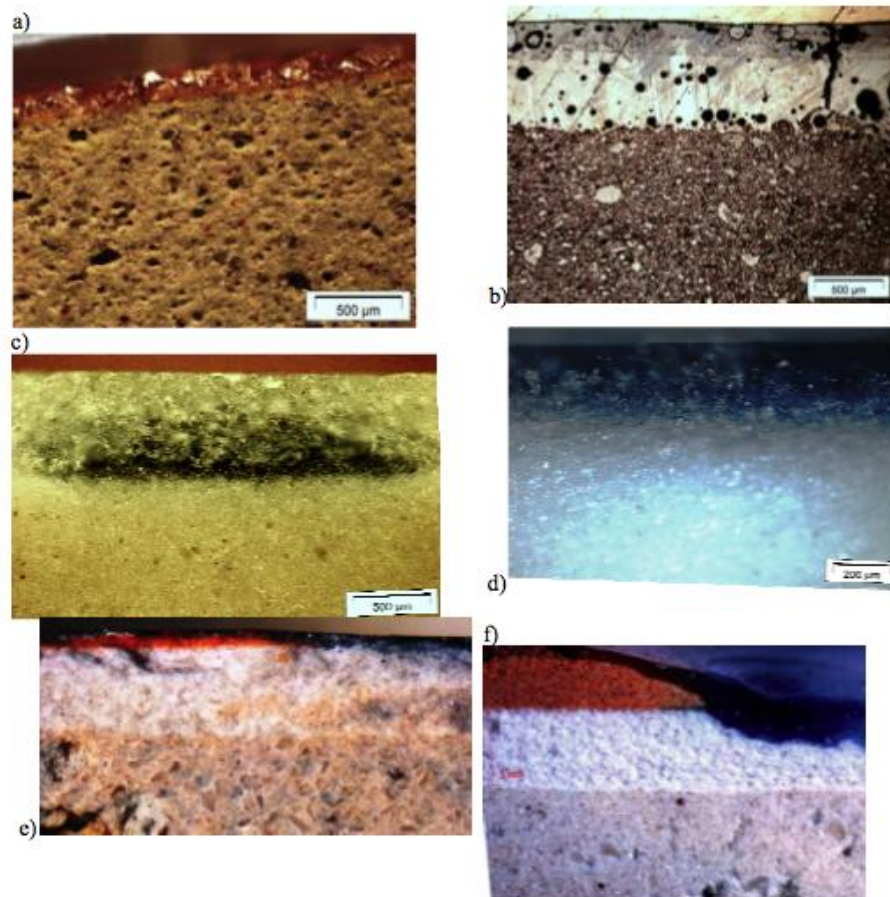


Fig. 7. Colour palettes. (a) of painting enamel (~200 mm in diameter) for Sèvres soft-paste porcelain (19<sup>th</sup> c.); (b) Ottoman Iznik polychrome dish decorated with red clove pink, ca 1575–1580; (c) Red flame glaze vase (end of 19<sup>th</sup> c., Sèvres Manufacture with crystallizations and detail of a Plant ash glaze made by Brother D. de Montmollin; (d) Lead-based glaze (Tran Dynasty, 14<sup>th</sup> c., Vietnam); (e) *fur hare* glaze (Courtesy Jean Girel, potter, 20<sup>th</sup> c.); Photos Ph. Colombar.

a)

b)



c)



d)



e)

f)



Fig. 8. Glaze coloured with metal nano-particles; (a) dish made by Eva Haudum, potter (note the golden and red shine for a given orientation; photo E. Haudum); (b) TEM images of a Fatimid lustre pottery (12<sup>th</sup> c., Egypt) and (c) of a 'pigeon blood' red glaze (courtesy of Ph. Sciau, CEMES-CNRS, Toulouse); (d) comparison of the visible-light absorbances of a glass with and without 0.25 wt % Cu metal nanoparticles.

