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Glaze and enamels

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Abstract

Glass coatings on potteries, glass and metals are used as décor but also for technical reasons, namely the tightening of porous bodies and hardening of their surfaces. The coating must be compressed and thus glaze-body thermal expansion mismatches, wetting properties and softening temperatures should be optimised. The glaze's thinness requires specific colouration techniques (pigments, metal nanoparticles). Consequently, the variety of compositions experimented on metals, potteries and glass substrates is very large. After a brief survey of glass coatings' characteristics (preparation, composition, coloration, thermal expansion, micro- and nano-structures), an overview of the history of enamels 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 proposed. The evolution of their preparation routes (ashes, rocks) and compositions is reviewed. The technical exchanges as well as the different techniques used to obtain similar visual effects are addressed with emphasis on the most innovative productions: Tang/Yuan/Song porcelain, Abbasid/Fatimid lustre pottery, Chinese/Vietnamese stoneware and *Celadons*, Japanese *Raku*, Iznik fritware, European soft-, hard- and hybrid-paste porcelains, 19th century technical revolution, Craft and Japonism movements, and Modern/Contemporary productions.

1. Introduction

Figs 1 and 2 show the variety of enamelled artefacts. A glass coating can be deposited on various substrates: a glass artefact (Figs 1a & 2c)[1], a metal (so called coat enamels or porcelain enamels, Figs 1d [2] & 2ab) [3,4], and a porous (*terra cotta*, faience, Figs 1b & 1f)[5] or a dense (stoneware Figs 1e & 2d, porcelain or fritware, Fig. 1c) ceramic [6,7]. Such coatings are often used for decoration purpose, but also for technical reasons: namely, the tightening of a porous body, the hardening of its surface and/or the improving of electrical insulation of wire supports in wet atmospheres [7]. First glazes have been deposited on stone in ancient Egypt [8] and enamelled lava continues to be used in contemporary building décor.

Different techniques are used to apply glass precursors (*in situ* reaction and melting) or glass powders (a frit previously prepared) on substrates. If the substrate is sufficiently porous (unfired or porous pottery) aqueous slurry is prepared and the enamel layer is obtained by dipping the object in the slurry, by spray-drying or by applying the mixture with a pencil. The slurry should have specific characteristics (viscosity, thixotropy, etc.) which are conditioned on the specific ingredients added (clays or kaolin, polymers). If the object is not porous, organic solvents/media generally replace water, 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. Ancient Egyptian used a special technique, taking advantage of an efflorescence phenomenon at the sample surface during the drying process to form an *in situ* layer of glass/colouring agent precursor.

Whatever the complex shape of the object, the glass layer thickness should remain equal and not form a puddle at the foot. Thus, it is evident that the enamelling technology covers a larger scope than the “simple” preparation and firing of a glass composition. Nevertheless 22th Egyptian Dynasty potters and Celts craftsmen still mastered enamelling on pottery [9] and metal [4] about 2.5 and 5 millennia ago, respectively.

It is not possible to cover in this short chapter all the varieties of enamels and glazes. After a brief survey on the preparation and technical characteristics required, and a presentation of the most pertinent innovations regarding composition and coloration, we will offer an overview of the history of enamels on metal, glass objects and potteries.

2. Definition, preparation and required characteristics

The coating should be rather small, from a few tenths of microns (salted stoneware) to a few millimetres (*Celadon*, *Cloisonnés*). To get a nice gloss and join with the substrate, a strong reaction should be developed during the firing process and the coating should have reached the molten state. It is thus mandatory that the precursor mixture consists in a fine powder. Grinding and firing are the two most energy consuming operations in *Arts du Feu* which might explain why grinding techniques only developed during the Middle-Ages. Consequently ancient craftsmen used alternatives to get fine powders: subsequent combination of firing of plants (ashes), shells and calcareous stone (chalk), bones (ashes), flint pebbles (silica) and water treatment led to very fine powders, sometimes with already the ‘good’ composition to directly enamel objects (Fig. 1e)[10,11]. The advancement of the phenomena taking place during the firing depends on the combination of the following parameters: initial compaction deposit, temperature, duration, heating rate, particle size, volatiles, and (reducing or oxydizing) gas atmosphere. A longer heating time has the same effect than a temperature increase because atomic diffusion drives the densification mechanisms: well compacted smaller particles react faster than bigger ones.

Controlling the contact angle between the molten coating and its substrate is mandatory to wet all places of the object but also to keep the thickness constant, both at the upper and

bottom part of the artefact. Formation of a bonding between the substrate and the coating is also very important. For metal substrate a ground or under coat is generally needed [7]. The most essential property of a ground coat is adherence to the metal substrate. Chief among adherence oxides are cobalt and nickel oxides. To a lesser degree, cupric oxide, manganese oxide and iron oxide may be efficient. Glazes for decorative purpose are then applied on the ground coat. Craftsmen know well that composition is not the sole parameter that governs the final quality [10-13]. For a same composition, the glaze can be obtained matt or glossy, well coated (Fig. 3c) or crawled (Fig. 3d) [11-13] as a function of the grinding time. Grinding can be conducted in a mortar manually, or in a barrel filled with water, glaze ingredients and flint/quartz pebbles (now steel, alumina or zirconia balls are used as a function of the glaze composition). A small quantity of clay or kaolin is generally added to control the viscosity and thixotropy of the glass precursor's slurry.

The huge variety of glaze compositions is imposed by that of substrates and their different thermal expansion and firing temperature. Glaze can be fired with the body (e.g. for porcelain, the firing temperature varies between 1200 and 1450°C, typically; this is the “*Grand Feu*” technique) or after, in a second (or third) firing cycle at a temperature sufficiently low to avoid modifications of the already fired (enamelled) body: they are called muffle firing, “*Petit Feu*” (Europe) or *mināi* (Iran); in this case the firing temperature ranges between 600 and 1000°C, typically) [13,14].

The thermal expansion coefficient of a metal substrate ranges between 220 and 100 10^{-7} K^{-1} (aluminium, 220; silver 195; brass/bronze/copper 180-160; gold 140 and steels 90-180 10^{-7} K^{-1}). Those of ceramic materials are smaller, even negative: β spodumene/eucryptite, -10 to -5; “amorphous” silica 1 to 10; SiC 35; mullite 50; porcelain 65; alumina 75 and zirconia 105 $\times 10^{-7} \text{ K}^{-1}$. However, quartz and quartz-rich bodies undergo a huge dilatation because of the α - β phase transitions at 565°C (200 to $>1000 \text{ } 10^{-7} \text{ K}^{-1}$ as a function of quartz content, Fig. 3a). Silicate glass thermal expansions ranges between 30 (borosilicate) to 80 (lead-based glass) $\times 10^{-7} \text{ K}^{-1}$. Adding silica, B_2O_3 , CaO, MgO, or ZnO at the expense of Na_2O and K_2O content reduces the glaze expansion [7]. Furthermore Bore addition increases the elasticity. We recall that the thermal expansion depends on the anharmonicity of the chemical bond and on the number of bonds per unit volume. The higher the bond strength/refractoriness is, the lower the bond potential anharmonicity and hence the lower the thermal expansion coefficient. Empirically the thermal expansion of a glass can be estimated using Seger' coefficients. Optimised calculators are available [15].

As for crystalline oxides the ultimate tensile strength of silicate glass is much smaller than the compressive one. Because of the coating's thinness, it should not be put under tension, but gently compressed by the substrate while taking into account the slow expansion that the porous ceramic body undergoes with time and while exposed to humidity. On cooling, below the softening point (Fig. 3a) and at the bonding temperature, the glass coating contraction is monitored by the thermal expansion mismatch [7]: to obtain a compressive stress the thermal expansion of the glass should be less than that of the substrate. On the contrary, a crackled glaze is obtained when the substrate expansion is low (Fig. 3b). A too high compressive strength leads to peeling.

The most common defects are volume bubbles, craters and pinholes due to 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 [10,11,13,16] for opacification or aesthetic effect.

3. Compositions and Microstructures

3.1. Pottery glaze

There is two different ways to present an object's composition: i) by its oxide or elemental composition (elemental composition is expressed in oxide wt % or in atom %), as determined *a posteriori* from elemental analysis (LA-ICP-MS, XRF, neutron activation, chemical analysis in the past) [17] - archaeologists and Art historian follow this presentation -, ii) by its raw materials composition which is preferred by professionals [7,10,11,18]. However glaze and enamel are not prepared by mixing "pure" oxides (an expansive and poor efficiency route) but by mixing (natural) raw materials: stones, clays, feldspars, talc, quartz, flint, carbonates, etc. The composition of natural compounds is highly variable, even from place to place in the same quarry. Consequently, craftsmen mixed materials from different places or better from very different origins in order to mean the differences and hence limit the fluctuations. Shifts in the raw materials composition require modification of the glaze composition and process. If the craftsmen were not able to adapt the compositions, the quality of the production would decrease and the factory disappears. Note that some compounds such as lead oxide are highly volatile and diffuse rapidly in the substrate. Consequently the composition obtained from elemental analysis is slightly different from that of the precursor. Potters and enamellers expressed compositions in wt % of the raw material and in oxide mole (Segger formula), for instance in Table 1 [10,14,18].

Low-firing lead-free glazes maturing at 1050°C (Segger Cone #2)¹ or less have one to two part silica per part of other ingredients. Higher-firing glazes melting at ~1250°C (Cone 10) have three to five parts of silica per part of others. High temperature fired porcelain glazes have ~10 parts or more of silica (Table 1).

The structural unit of silicate, the SiO₄ tetrahedron shares all oxygen atoms in pure silica, forming a strong 3 dimension strongly bonded covalent polymeric network (Fig. 4a). In order to weaken the melting temperature of silica (~1740°C) as well as the viscosity of the melt, glazemakers replaced some silicon atoms developing strong covalent Si-O bond by alkali/earth alkali (Ca, Na, K, Li) or Pb atoms forming less strong ionic bond. This induces a depolymerisation of the framework as in the crystalline tecto-phylo/cyclo-inno-nesosilicate sequence encountered in crystalline natural minerals [18-20]. On the other hand addition of aluminium increases the melting temperature, the viscosity and the chemical stability.

Raman spectroscopy analyses directly the chemical bond and Raman parameters, for instance the ratio between SiO₄ bending mode vs. SiO₄ stretching mode area (Fig. 4b) measures the polymerisation degree: very low for full depolymerised lead-rich glass (melting temperature ~700°C) and at the maximum for 3D connected silica-rich glaze (melting temperature ~1400°C, Figs 4 c & d) [18-20]. A direct relationship can be established with the melting temperature. This illustrates very well the huge variety of polymerisation degrees and compositions synthesized by craftsmen to reach the required properties. Similar behaviour is observed for natural crystalline silicates and phosphates (Fig. 4c) [20].

Professionals prefer to use the Seger formula [7,10,18]. This formula distinguish acid (SiO₂), amphoteric (Al₂O₃) and basic (flux: CaO, Na₂O, K₂O and MgO) oxides [7]. Balance between the different oxides determines the physical and chemical characteristics. Table 2 illustrates the huge variation of glass compositions with firing temperature from ~600°C (Cone 022) to ~1430°C (Cone 15). The choice of the raw materials (and not the mean composition) determines the temperature at which the first liquid phase is formed, an important parameter for coating reacting/bonding with the substrate.

Note that the firing cycle's duration has been drastically reduced during the 20th century. Up to the 1960s the duration of a complete cycle (heating & cooling) can exceed several days. A

¹ The advancement of reactions and atom diffusion depend both on temperature and time. Seger cones are specific mixtures designed to deform and melt according a controlled firing (temperature and heating rate). They cover the temperature range between 500 and 1520°C [15].

week was common in 19th century and many weeks necessary for Chinese Dragoon medieval kilns. Replacement of isolation brick walls with oxide fibre felts in the 1980s reduced the firing cycle to a few hours or even a few tenths of minutes for firing tiles.

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) [7].

3.3 Micro- and nano-structures

Figure 5 shows representative microstructures: thin (Fig. 5a) and thick (Figs 5b, 5e & 5f) glaze layers, single (Figs 5a & 5c) and multi (Figs 5b, 5e & 5f) glaze layers. Iznik fritware section shows a good example of complex multilayered glaze obtained by many firing sequences. Thinner glassy coatings are obtained by the salting technique: NaCl, lead oxide or plant ashes are poured 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 (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.

The glaze being 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: painting directly 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 by adding a highly refractory material (chromite or spinel, e.g. in Timuride and Iznik productions, Fig. 3e; hematite in Mamluk glass enamelled artefacts, Figs 3c & 3d). Furthermore, the hematite matt layer can be used as a rough substrate to physically attach the thin gold foil [12]. Another notable property of non-stoichiometric structures such as spinels and chromites is their ability to catch diffusing ions.

Actually many glazes contain micro or nanocrystalline secondary phases and belong to glass-ceramics materials. Indeed, if the particle size is inferior to 1 μm the optically clearness is kept. This is the case for calcium-rich glaze with wollastonite precipitates, common for Chinese and Vietnamese stonewares and *Celadons* [11,16,21-23] as well as for 18th century soft paste European porcelains []. Growth of the crystalline second phase led to specific décor, largely experimented at the end of 19th century and in contemporary creation (Fig. 6d') [10]. Another type of nanoprecipitates is metal nanoparticles used as colouring agents (see below)

4. Colouration

Colouration of transparent matrixes is obtained by addition/dispersion of colouring agents (Figs 1-3 & 5-7). Indeed the colour perceived by our eyes arises from the light not absorbed by the glaze. Four methods allow colouring a medium.

- i) The simplest type of agent colouring a glass matrix is an ion with electronic transitions in the visible range, namely a Transition Metal (Fe, Co, Cu, Mn, V ...) or a Rare Earth ion (Pr ...). The ion is located in empty sites within the glass network (Fig. 4a). Typically a concentration of 0.1 to 1 wt% of metal is sufficient for an efficient coloration. The hue depends more or less on the occupied site and glass matrix composition: the most important

effect is for Cu^{2+} ion which leads to turquoise colour in alkali glasses (Fig. 3e) but green in lead-based ones (Fig. 6e). Colouring powers achieved this way are limited, especially for thin films, thus other routes have been developed [7,10,11-13,22,24-28] (Tables 4 & 5).

- ii) A crystalline matrix can be specially prepared to host colouring ions and enhance colouring efficiency and tuning precision: the pigment is synthesized independently and then incorporated to the glass. Alternatively, saturation in certain element leads to precipitation of phase(s) on cooling. The reactivity of the pigment should be sufficiently weak to avoid its dissolution/modification in the molten glaze. Phases with compact structures and high refractariness such as spinels, corundum, garnets and zircon form good matrices (Tables 4 & 5) [28].

Ancient pigments usually belong to silicate and lead-based compounds. The same structure has been used by Egyptian and Chinese craftsmen to prepare blue pigments, but with different earth-alkali cation, Ca and Ba, respectively. Natural pigments, such as Lapis lazuli, a feldspar (lazurite) coloured because of its doping by S_x ions (Figs 3c & 3d), have been used at least since Ptolemy Dynasty to colour pottery glaze and glass object enamels [12]. Sixteen century after, J.F. Böttger took advantages of the high colouring power of lapis lazuli to whiten the glaze of first European porcelain (Meissen Factory, Fig. 2f, [28]). Alternatively, secondary phase precipitation can be tailored to opacify the glaze: by this way cassiterite (SnO_2), fluorite (CaF_2), calcium antimonate, lead arsenate and phosphates opacify the glass [10,12-14,28].

- iii) A third way is to use metal nanoparticles (formerly called colloids) as pigments or as diffracting agents. The light absorption arises from its interaction with 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 the electron gas, and the broader features to interband electronic transitions. [25] Typically, particles of gold, copper, silver and iron led to ruby, red, yellow and grey colours, respectively. Glaze coloured with colloidal gold is called Cassius purple [28]. Formation of metal nanoparticles requires the control of redox equilibrium within glass, which is achieved either – directly – by firing under hydrogen (produced by wet wood), a gas which diffuse easily in the glass network, or – indirectly – by the fast diffusion of multivalent ions reduced at the glaze/enamel surface ($\text{Fe}^{3+/2+}$, $\text{Sn}^{4+/2+}$, $\text{Sb}^{5+/3+}$, $\text{Eu}^{3+/+}$, ...) [5,25,29]. *Jun, flammé* and Art Nouveau pottery are 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) [30,31].

- iv) A fourth very advanced method of colouration is based not on the absorption of the light but on its diffraction. The technique is largely used by Mother Nature (opals, mother of pearl, butterfly wings, beetles, cephalopods, tridacna...). The colour arises from constructive/destructive interferences formed by the nanoparticles organisation at the layer level. The technique is called lustre (Figs 1b, 6f & 7a) and date from Abbasid Dynasty (9th century) [5,25,29]. The alternation of metal particulates' rich and free layer is achieved by controlled sequences of oxidising/reducing atmospheres at the pottery surface.

-v) The last method to colour a glass artefact, called gilding or silvering, is to coat with a coloured metal layer (Au, Figs 1a, 2a, 2b, 2d, 3c (traces) and 3f) or with silver (Ag). Brass and mercury alloys are also used [25]. The metal layer can be physically (taking advantage of the rough surface) or chemically bonded. Different techniques, initiated during the Renaissance are possible (addition of Bi_2O_3 , resinnates, etc.).

White colour is obtained by dispersing a second phase with a grain size comparable to that of the visible light wavelength and with an optical index different from that of the glass matrix, namely bubbles, quartz, cassiterite (Figs 1b, 1c, 3e & 6c), fluorine (Fig. 1d), calcium phosphate, lead arsenate, zircon and zirconia.

Because of the rather small quantity of colouring elements used, elemental analysis is not very efficient to identify the colouring agents or requires very localized (destructive) analyses

[32]. Raman spectroscopy, especially when the exciting laser wavelength led to resonance Raman Effect, and diffuse Reflectance spectroscopy are the most efficient techniques [20,22,28,33].

Figs 6a and 6b shows colour palettes on porcelain of the very end of 18th century and of the middle 19th century of the Sèvres Manufacture [14,22,24]. The enamels have been painted with different thicknesses. Different colour hues arise also from small modifications of the glaze composition [13,14]. The higher the firing temperature, the more difficult is the conservation of a large palette of shades.

Glaze demixing is tailored for special effects, e.g. aventurine flame (Fig. 6d) or fur hare (Fig. 6f) glaze, sometimes in combination with the formation of copper or iron metal particles, respectively [30].

4. A brief historical overview

4.1 Enamels on metals

In Western Countries the first use of glassy silicates as enamel on metal seems to date back to at least 1500 B.C. in Cyprus [3]. A famous mention is present in the Iliad (8th B.C.) in the form of an enamelled shield. Also, an enamelled bronze wine ladle from the early Western Zhou dynasty (11th century B.C.) is at the British Museum. Celts produced large quantities of enamels on brass, bronze, gold and iron (>4th B.C.). Five colours are currently made: blue, red, green, yellow and black [4]. Then *millefiori* enamels appeared in Ireland during the 7th c. The craftsmen of those early artefacts had first solved the viscosity control by the *champlevé* technique, where carving the metal substrate formed rifts which retained the molten glass in the pattern of the decoration during the firing. More intricate decors were achieved during the 2nd century B.C. through the replacement of the carved regions with thin walls made up of metal foils called *cloisons* (a thin metal strip perpendicular to the substrate delimits the different coloured areas and forms depicted, Fig. 1d). The first ones were made by Celts on various metals and at 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' Empire (6th – 11th century). During the 12th and 13th centuries, Limoges (France) and Silos (Spain) were big production centres, in relation to *al-Andalus* Muslim culture. Silver substrates were used in Italy from the 14th century onward.

A medieval Chinese report calls the enamelled work *guiguo yao*, a production from the 'devil countries', i.e. the western countries [2]. When the production of *cloisonné* enamelled objects developed in China (~>16th century, Fig. 1c), the *cloisonné* technique had almost disappeared in Europe (up to the renewal at the end of the 19th century with Japonism and Craft Movements) following the emergence towards the end of the 15th century at *Limoges* [3] (Fig. 2 a&b) of a new technique called 'painted enamelling'. This technique was also in use in Burgundy and the Netherlands, as well as in other parts of France and Europe during the same time period. Painted *Limoges* enamels display an elaborate technique with multi-layer paintings of enamel on a copper support involving numerous firings and different sets of enamel compositions (Figs 2a & 2b). The back side is also enamelled. This technique called *falang* in China (a homonym of the Chinese word for 'France') was more sophisticated than the earlier metal enamelling techniques such as the *cloisonné*, wherein there is no need to have series of glassy compositions and the same glassy matrix can be used for different colours. Note that the artefact must be polished after firing. The craftsmen depicted very complex motives from episodes of antic legends or the Bible, like the potters of the *majolica* ceramics. Besides polychrome works, around 1530–1540, a new type of enamel, named *grisaille*, employed limited colours, mainly black and white, to enhance the visual effects in the flesh areas of the human figures depicted. During the 17th century, the quality of the

enamels had started to decrease until a remarkable revival took place in the 19th century: the workshops not only produced modern *Limoges School* pieces, but replicas of Renaissance enamels were also often being sold as originals (Fig. 2b [3]).

4.2. Pottery Glazes

In Western countries, glazed artefacts date back to ~1500–2000 B.C. (Egypt, Phoenicia, Mesopotamia and Indus Valley), especially those coloured/opacified with lead antimonate yellow, and calcium antimonate white [9,28,31]; and where some were produced by the efflorescence technique (turquoise glaze on quartzite or on synthetic silica body) [8,9]. Heating at ~900–1000 °C was achieved. At the same time, in Eastern Countries, Chinese Shang and Shang-Zhou proto-porcelains (3000–1500 B.C.) were fired at temperatures up to ~1200–1250 °C [21].

Roman potters (*sigillata*) and glassmakers experimented mass production. The colouration of the surface layer, a layer with characteristics intermediate between a glaze and a slip, was coloured with hematite, hercynite or pseudobrookite [32].

Chinese Eastern Han to Sui potters (2nd B.C. –7th c.) initiated the development of very high temperature firing technology: indeed, Yue wares were fired above 1300 °C [11,21]. The first glazes obtained using plant ashes were used as décor (Fig.1e) in a fashion that looked very modern from an aesthetic point of view.

White porcelains appeared during the Sui and Tang Dynasties (7th–8th c.) [21]. At the same period Islamic potters found how opacification by cassiterite tin oxide, a Roman glass maker technique (5th c.), combined with low temperature firing could compete with high temperature fired porcelain to produce artefacts with complex depictions [5,29,31]. 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 [29]. The chemical reaction between the two glazes led to precipitation of white cassiterite [28]. The use of cassiterite opacifier spread around the Mediterranean Sea with the expansion of the Islamic World (*Ifriqaya* (7th c.), *al Andalous* (8th c.), Sicilia (9th c.)) and then to Italy (*majolica*, 13th c.) and France (15th–16th c.) [26,27,29]. Table 7 illustrates the composition shift from calcium-rich Chinese Five Dynasties glazes to potassium-based Song glazes. Similar evolutions took place in Vietnam from the Ly to the Tran Dynasties [16] but with some delays.

Blue-and-white Yuan porcelains were first prepared using cobalt pigments imported from Europe, taking advantage of the Mongol Empire Pax along the Silk Road. Then local sources were used. These Asian cobalt ores contained a large amount of manganese and iron that required strong reducing firing atmospheres to only develop the blue colour desired [16]. Fortunately Chinese and Vietnamese potters well mastered the kiln atmosphere, especially using coal as fuel. Blue decor can be 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 were achieved in Anatolia; Ottoman Iznik manufacture(s) developed fritwares from ~1450 to ~1620 (Figs 5 e&f and Fig. 6c [6]). In Italy the Duke of Medici's porcelain (Fig. 2e), a hybrid porcelain intermediate between fritware and hard-paste China, was produced from ~1575 to 1587 with the help of a Master coming from the Levant [34]. One century after (at the end of 17th century) soft-paste porcelain (silica-rich body made a quartz grain cemented with a glass, a sort of fritware) Manufactures appeared in France (Rouen, Saint-Cloud, Chantilly, Vincennes, Tournai, Mennecy) and then hard-past porcelain Factories (Fig. 1 a&b) developed in the whole of Europe (Meissen, Strasburg, Vienna, Saint-Petersburg ... [22,28,35]). Hard-paste porcelain also called China is made with kaolin and feldspar: this

is an alumina-rich body transformed in acicular mullite crystal frame (~30 % in volume) soaked with a glassy matrix. The major difficulty was the building of a kiln able to reach and to be maintained a few days at 1450°C. Consequently the first tentatives to fire porcelain used solar beam and lenses! Iznik potters first used 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 & 5f). These grains act as a reflector for the light leading 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. After that, Kütahya's manufactures (Fig. 1c) maintained the creativity of Ottoman glazed fritwares [6]. Ottoman potters produced multilayer glazed artefacts requiring multi firing cycles (Fig. 5 e&f). The soft-paste porcelain route, can be considered as an evolution of the Iznik fritware technology (the body consists in quartz grain cemented with the frit)

The availability of kaolin allowed for the preparation of hard-paste alumina-rich porcelain. Its high refractoriness led to design new glaze compositions. A revolution took place after 1750 with the development of faience and porcelain factories in Europe [22,28].

White elegant Song porcelains were largely exported, including in Japan. But, throughout the 13th to 16th centuries, some scholars start to prefer Chinese and Vietnamese stonewares. Their more brut habits was better prized than the very aesthetic Song style, according to the *wabi-sabi* Movement and the development of the Tea Ceremony [36]. During the Momoyama period, local potters, in particular those of the Raku Family, already very active, developed a highly original style. Unpredictable kiln effects (i.e. defects!) were cultivated and these "accidentally lovely" works used as flower vases and as utensils for the Tea Ceremony [36]. The discovery of this production at the firsts *Expositions Universelles* led to the *Japonism* and *Craft* aesthetic Movements. They remained dominant in a large part of the contemporary pottery production.

Another technical revolution occurred during the 20th century with the development of advanced ceramics, in particular dielectric passive components (capacitors, substrates, sockets, *etc.*) at the root of the development of microprocessors and computers. Glazes were designed to be deposited on some alumina electronic substrates to be used in standard or harsh conditions [7]. Iron oxide-rich enamels were used to coat porcelain or glass isolator for high voltage electric line and transformer.

4.3. Enamels on glass

High quality glass artefacts have been produced in large quantities since the beginning of Roman times.[1,12] Among this production, very rarely are dichroic/lustre and enamelled glass reported in ancient literature [13] represented in Museum collections [1,12,37]. Amidst the major examples of preserved enamelled glass objects are what remains of the Afghan Begram Treasure (1st century AD), the fragments of the Lübsow cup found in Poland (2nd century AD) and the Cohn Beaker & Hans Cohn Collection, which is supposed to have been found in Egypt [12,37]. Besides those, and up to the Islamic and Venetian productions of the 13th century, the evidence becomes infrequent. The few remaining pieces representative of the whole Byzantine period are: a group of gilded and occasionally enamelled vessels from Corinth and Paphos together with a series of sparse objects, all dated between the 10th and the 11th century, and the famous San Marco Bowl also dated to the 10th/11th century and probably brought back to Venice from Constantinople in 1204. Then, the enamelling and gilding technologies developed at the Normand/Swabian Frederician Court (recent excavation at Melfi Castle, South Italy, 13th century) and during the Ayyubid and the Mamluk period in Syria and Egypt [12] produced pieces exported all over the ancient World, from Europe to China. Mameluk Mosque lamps, mostly hanging lamps, are among the most magnificent evidences of the technical virtuosity of those glassmakers. The use of lapis lazuli, a semi-

precious stone, as ceramic or glass pigment was longtime rejected by the scholars. Recently, it was demonstrated that lapis lazuli powder, sometimes mixed with cobalt ore, was largely used to colour pottery glazes and glass enamels during the 14th century [12]. Furthermore, the ancient use of those components, up to the 1st century or even before (Glass Begram Trésor, Musée Guimet, Ptolemaic glazed pottery from Pompeii) was confirmed [12].

The development of chemistry at the end of the 19th century offered a variety of routes to colour a glass matrix and enamels. In France Philippe-Joseph Brocard and Emile Gallé were very innovative craftsmen. Representative masterpieces are shown in Fig. 2c. Brocard's approach, the mixing of a variety of colouring agents, may be related to his self-teaching of glass making, as opposed to the more traditional glass technology – he was not educated as a glassmaker like Gallé – and his expertise in various fine arts was very representative of the 19th century technical innovation spirit. On the other hand, Gallé took advantages of his traditional glass making expertise in order to create new forms, with innovative shape and colour association, contributing to the novelty of Art Nouveau aesthetic. The most striking innovations at the turn of 19th / 20th century are the use of $\text{CdS}_{1-x-y}\text{Se}_x\text{Zn}_y$ semiconductor nanoprecipitates to prepare vivid red to yellow and of UO^{2+} ions for yellow glaze [7,33].

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Table 1: Examples of modern porcelain glaze composition expressed in oxide and raw materials wt% [after Colombari & Paulsen [18]]

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

* English China Clay (St. Austell, UK); ** Dorfner (Hischau, Germany); ***North cape Minerals (Stjernoy, Norway); ⁺Partek (Helsinki, Finland); ⁺⁺ Norwegian talc (Bergen, Norway)

Table 2: Representative modern glaze compositions expressed with Seger formula (after Epler & Epler [7])

Glaze type	Cone	Acid	Amphoteric	Basic (Flux)				SrO	Li ₂ O	K ₂ O	Na ₂ O	ZnO	B ₂ O ₃	PbO (P ₂ O ₅)
		SiO ₂	Al ₂ O ₃	ZrO ₂ (SnO ₂)	Fe ₂ O ₃	MgO	CaO							
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	0.0113					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	0.2682
	010 <022	0.6599	0.0719										0.1831	0.2958
Aventurine	4	0.5795	0.0886		0.0453	0.0407	0.0724		0.0277	0.0954	0.0524			0.5211
Crackle	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	6	0.7422	0.0918		0.0029	0.0065	0.1206		0.0345	0.0011				(0.0005)
Chun/Red	8	0.7718	0.0619		0.0064	0.0237	0.100		0.02604	0.0072				(0.0022)
Ash	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 Epler & Epler [7])

Enamel type	Tp °C	Acid	Amphoteric	Basic (Flux)										
		SiO ₂	Al ₂ O ₃	ZrO ₂ (TiO ₂)	Fe ₂ O ₃	MgO	CaO	NiO (CoO) (0.0101 (0.0045))	Li ₂ O	K ₂ O	Na ₂ O	ZnO (BaO) (0.0186)	B ₂ O ₃	F (P ₂ O ₅)
Ground coat	805	0.4987	0.0382			0.0013	0.0718		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 presently used (20th-21th century)

Pigments	Structure	Colour
$\text{Co}(\text{Al},\text{Sn})_2\text{O}_4$	Spinel	Blue
CoSiO_4	Olivine	Blue
$\text{CoAl}_x\text{Cr}_{2-x}\text{O}_4$	Spinel	Blue-green
$(\text{Zn},\text{Fe})(\text{Fe},\text{Cr})_2\text{O}_4$	Spinel	Black
CuCr_2O_4	Spinel	Black
$\text{Zn}(\text{Al},\text{Cr})_2\text{O}_4$	Spinel	Pink
$3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3 \text{SiO}_2$	Sphepe	Victoria Green
$\text{Pb}_2\text{Sb}_{2-x}(\text{Sn},\text{Si},\text{Fe}..)_x\text{O}_7$	Pyrochlore	Naples yellow
$\text{ZrSiO}_4:\text{V}$	Zircon	Blue
$\text{ZrSiO}_4:\text{Pr}$	Zircon	Yellow
$\text{ZrSiO}_4:\text{Fe}$	Zircon	Pink
$\text{ZrO}_2:\text{V}$	Zircone baddeleyite	
$\text{SnO}_2:\text{V}$	cassiterite	yellow
$\text{Al}_2\text{O}_3:\text{Cr}$	corundum	Ruby
$(\text{Al},\text{Cr})_2\text{O}_3$	corundum	Red
Cr_2O_3	corundum	green
$\text{Fe}_{2-x}(\text{Al},\text{Ti},\text{Mn})_x\text{O}_3$	Hematite (corundum)	Red
$\text{Fe}_{2-x}\text{Al}_x\text{Ti}_x\text{O}_3$	Hercynite (spinel)	Red
$(\text{Co},\text{Ni})\text{O}$	Periclase	Gray
$(\text{Co},\text{Zn})_2\text{SiO}_4$	Phenacite	Blue
$(\text{Ti},\text{Ni},\text{Nb},\text{Cr},\text{Sb})\text{O}_2$	Rutile-Cassiterite	Brown
$(\text{Sn},\text{V})\text{O}_2$	Rutile-Cassiterite	yellow
ZrSiO_4	Zircon	White
ZrO_2	Zircone	White
$\text{CdS}_{1-x}\text{Se}_x$	Wurtzite	Yellow (S) to red (Se)

Table 5: Main ancient pigments

Pigments	Structure	Composition	Colour	Date
Lazurite (Lapis Lazuli)	Feldspathoid	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}:\text{S}_x$	ultramarine	Roman
Ultramarine	zeolithe	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}:\text{S}_x$	ultramarine	> ~1830
Co-olivine	olivine	Co_2SiO_4	blue	>1500
Sèvres blue	Spinel	CoAl_2O_4	blue	>18 th
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		Ca_2PO_4	white	Roman
Rutile	Rutile	TiO_2	white	>20 th
Quartz	quartz	SiO_2	white	>5 th
Tin oxide	Cassiterite	SnO_2	white	>5 th
wollastonite		$\text{Ca}_3\text{Si}_3\text{O}_9$	white	>18 th
Arsenate		$(\text{Pb},\text{Ca})\text{AsO}_4$	white	>16 th
Uranyl yellow		UO^{2+} in (lead)glass	yellow	>19 th
Cadmium sulphide-selenide	Wurtzite	$\text{CdS}_{1-x}\text{Se}_x$	Yellow to red	>20 th
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	ZnCrO_4	Yellow	>19 th
Mussif Gold		SnS_2	Gilding	>13 th
Hercynite	Spinel	$\text{Fe}_{2-x}(\text{Al},\text{Ti},\text{Mn})_x\text{O}_3$	Orange	Roman
Hematite	Corundum	$\text{Fe}_{2-x}(\text{Al},\text{Ti},\text{Mn})_x\text{O}_3$	Red	Roman
pseudobrookite	brookite	$\text{Fe}_{2-x}(\text{Al},\text{Ti})_x\text{O}_5$	Red	Roman
gold	Metal nanoparticle	Au	Red	15 th
Copper	“	Cu	purple	
Silver	“	Ag	red	<5th B.C.
			yellow	12 th

Table 6: Examples of mean composition of enamels on metal substrate (after Kirmizi et al. [2,3]).

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

Table 7: Examples of mean composition of glaze layers on terra cotta, stoneware, hard- and soft-paste porcelain bodies (after [11,16,21,23]).

Type	Origin / century	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	PbO	P ₂ O ₅	Fe ₂ O ₃	TiO ₂	MgO	B ₂ O ₃ (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 th	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 th -13 th (Longquan)	67	14.5	10	5	0.5	-	0.6	0.5	0.1	1	
	Hard-paste	Northern Song 12 th (Jun)	71	10	10	3	0.5	-	0.5	<2	0.4	1.5
Northern Song 10 th -13 th (Ding)		72	17	3	2	0.5	-	-0.2	0.5	0.2	2.3	
Vietnam 15 th		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 th		61	33	4.8	0.1	0.2						
Meissen 18 th		59	35	0.3	4	0.8			0.3	0.1		
Terre de Lorraine 20 th		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	
Soft-Paste		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	
	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: Examples of the variety of glass coatings; a) enamelled Venetian chalice (circa 1480-1500), b) glazed Ottoman Kütahya bowl (end of 17th century); c) Hispano-Moresque Lustre pottery (15th century); d) Chinese cloisonné (16th century); d) Han Viet pottery glazed with ashes (before 6th century); e) Raku tea bowl (20th century) voluntarily broken and restored using the golden lacquer technique (courtesy of Andoche Praudel Potter); Photos Ph. Colomban.

Fig. 2: Limoges enamels. a) Plaque depicting Jesus in front of Ponce Pilate tentatively assigned to Penicaud (16th/17th century, UCAD Coll.), partially restored; b) Plaque depicting King Henry IV, initially dated from 17th century, actually a 19th century fake (UCAD PE1640) []; c) Gallé' enamelled glass (UCAD Coll); d) Sceaux porcelain ewer decorated with Cassius Purple enamel (MNC Sèvres Coll.); e) Medici porcelain plate (16th c., MNC Sèvres Coll.); e) Rhino from Pilnitz garden (J.F. Böttger, Meissen, early 18th c., MNC Sèvres Coll.), Photos Ph. Colomban.

Fig. 3: Control of the glaze quality. a) 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); b) Celadon crackled glaze (19th century, Qing Dynasty); c) High quality Mamluk enamelled glass bottle exhibiting a high qua(14th century); d) Mamluk enamelled mosque lamp where the glaze has failed to adhere to or wet the body on firing (crawling); e) *Cuerda seca*-like technique : a line hinders the glaze to go out of the defined area (15th century, Ottoman Empire) [6]; f) micro-crazed red glaze of a gilded Meissen Böttger' stoneware; Photos Ph. Colomban.

Fig. 4: a) Schematic of the glass polymeric network made of more or less connected SiO₄ tetrahedron with fluxing ions in between; b) Typical Raman spectrum showing the stretching and bending components relative of the different types of tetrahedron (Q₀, isolated to Q₄ full connected), the Boson contribution has been subtracted [19,20]; Plot of the polymerization index (ratio of the bending vs. stretching band area) for crystalline (c) and amorphous (d) silicates; the main flux and other oxides are indicated, after [19,20,24].

Fig. 5: Representative optical microscope view of sliced sections of glazed potteries (b, polished). a) Lead-rich glaze on terra cotta body (14th century, Oman Sultanate); b) Ottoman lead-alkaline glaze on clay-rich body tile tempered with quartz grains (15th century); c) Chinese glazed stoneware with under-glaze dark blue décor (15th century); d) Chinese blue over-glaze décor on porcelain (17th century); e) Ottoman Iznik glazed tile: note the 3mm thick white quartz grain-rich slip over the body (fritware) and the multilayer glazed blue and red overglaze (16th century); e) detail; Photos Ph. Colomban except e & f, Courtesy G. Simsek).

Fig. 6: Colour palettes. a) Palette (210 x 210 mm) of used painting enamels ('Petit Feu' 880 °C firing) on Sèvres PDN hard-paste porcelain (19th century); b) palette (~200 mm in diameter) of painting enamel on Sèvres soft-paste porcelain (19th century); c) Ottoman Iznik polychrome dish decorated with red clove pink, ca 1575–1580; d) Red flame glaze vase (end of 19th century, Sèvres Manufacture with crystallizations and detail of a Plant ash glaze made by Brother D. de Montmollin); e) Lead-based glaze (Tran Dynasty, 14th century, Vietnam); f) '*fur hare*' glaze (Courtesy Jean Girel Potter, 20th century); Photos Ph. Colomban.

Fig. 7: Glaze coloured with metal nano-particles; a) dish made by Eva Haudum Potter, note the golden and red shine for a given orientation (Photo Eva Haudum); b) TEM image of a Fatimid lustre pottery (12th century, Egypt) and c) of a '*pigeon blood*' red glaze (courtesy of Ph. Sciau, CEMES-CNRS, Toulouse); d) comparison of the UV-visible-nIR absorbance of a glass with 0.25 % wt Cu metal nanoparticles and without.

a)



b)



c)



d)



e)



f)



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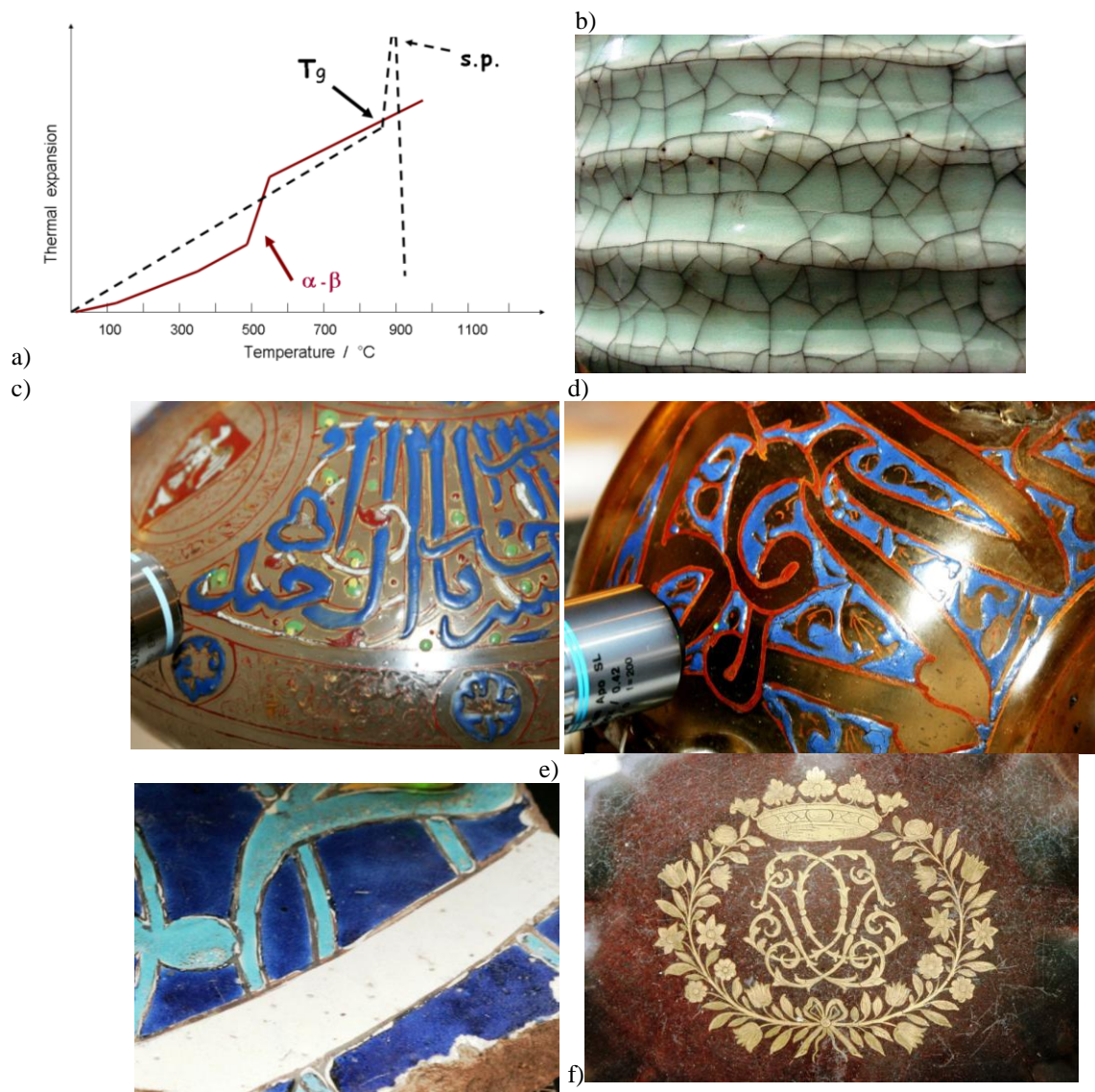


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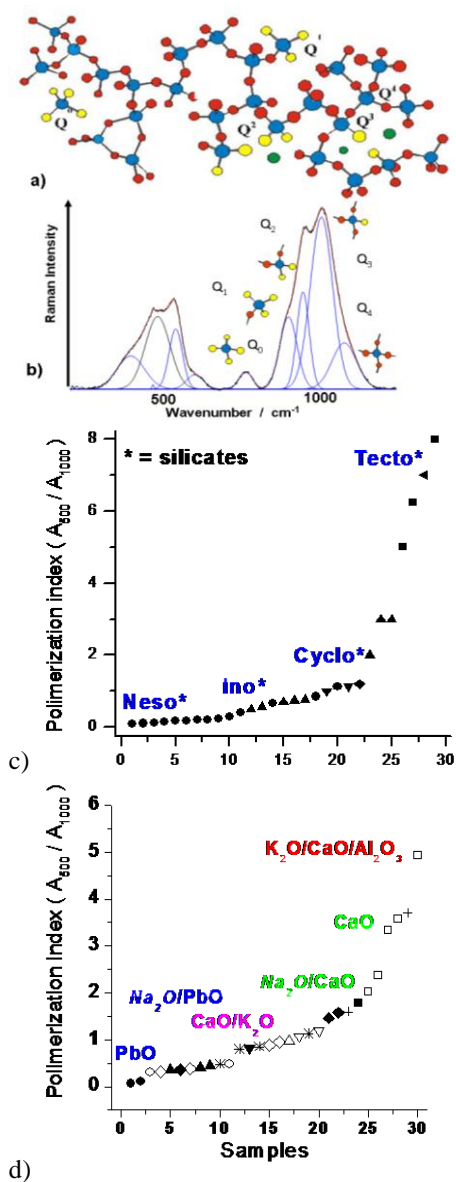


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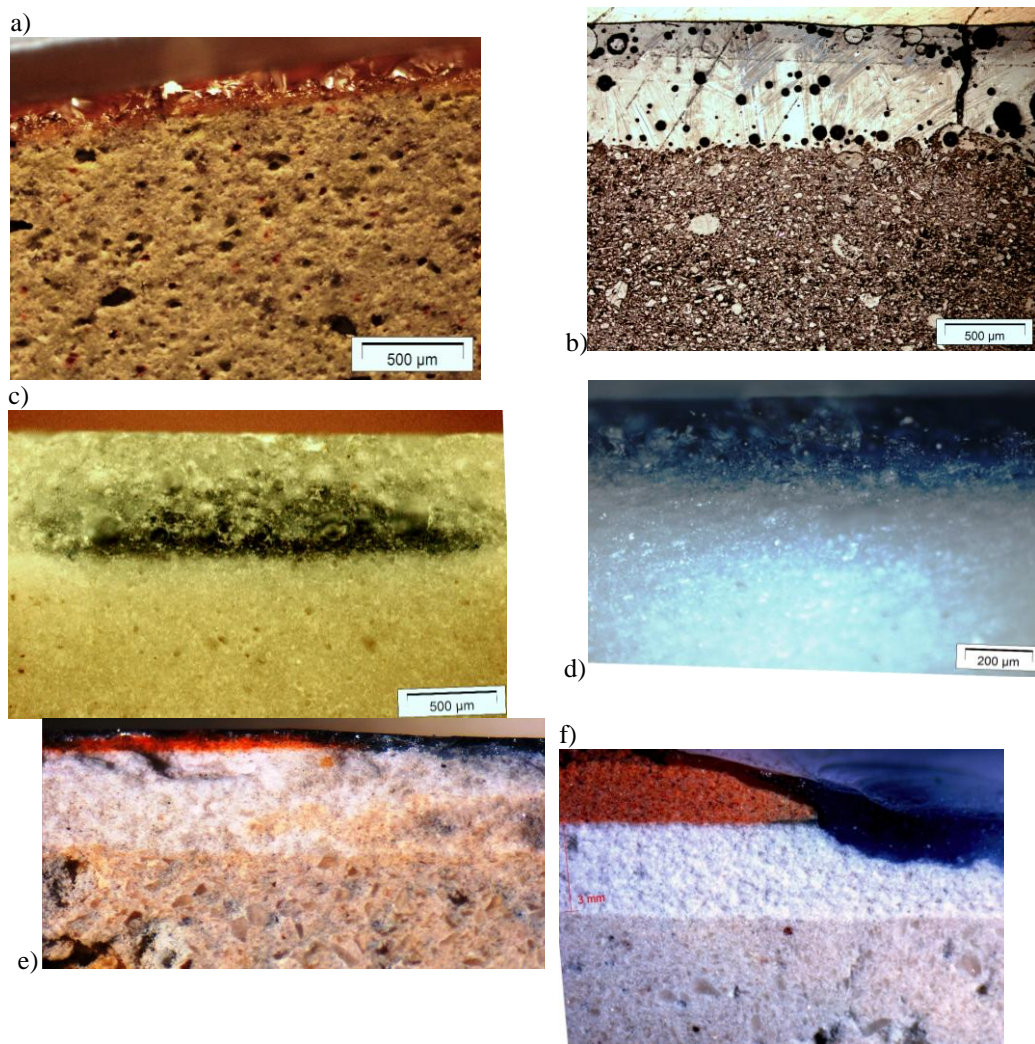


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a)

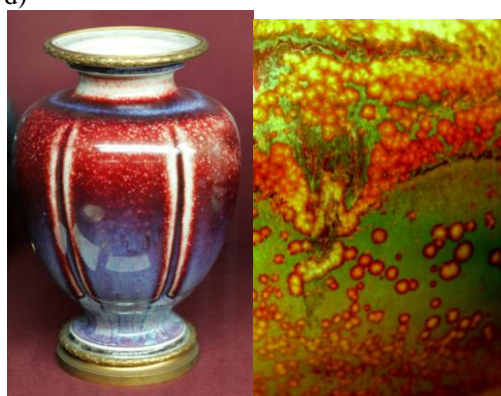
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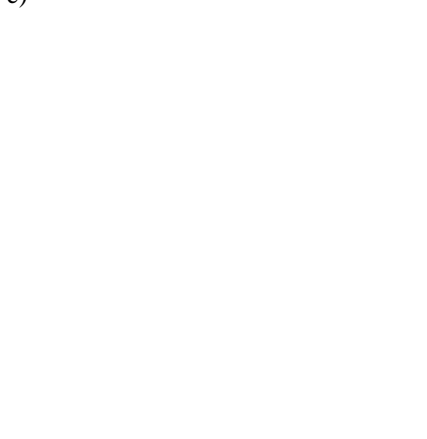
c)



d)



e)



f)



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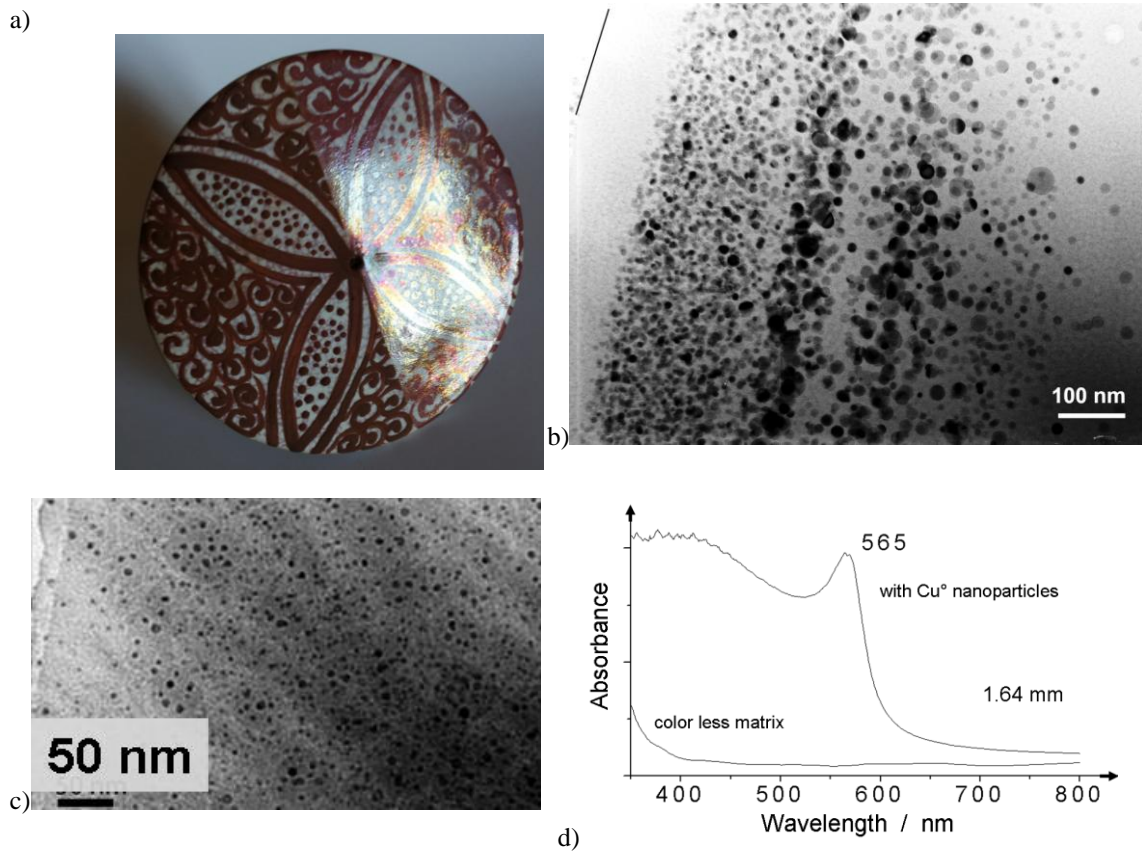


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