



Glass-based pigments in painting: smalt blue and lead–tin yellow type II

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Abstract

Glass-based pigments have an important role in the panorama of artistic production due to the fact that their manufacturing processes involve a combination of different skills and understanding, and they have a role in disciplines ranging from glass technology to metallurgy, from glazed ceramic to stone imitation and from vitreous mosaic tesserae to painting materials. The main goal of this manuscript is to present a critical review of the literature relating to blue smalt and “yellow glass” (lead–tin yellow type II) pigments: presenting their historical background, the analytical protocol, the processes of alteration and decay and finally tracing issues. Several case studies analyzed by the authors will be presented. Particular attention was devoted to the correlation between micro-textural features and decay processes affecting the studied pigments, though the widespread heterogeneity of the analyzed materials and the variability of the artistic techniques in which the pigments were used as well as the effect of the relevant (micro-)environmental conditions dictate a cautious approach. These studies are presented in the context of information about the chain of production, the selection of the raw materials and relevant provenance studies.

Keywords Glass-based pigments · Zaffre · Smalt · Lead–tin yellows · Degradation · Analytical protocol

Premise

This Topical Collection (TC) covers several topics in the field of study, in which ancient architecture, art history, archaeology and material analyses intersect. The chosen perspective is that of a multidisciplinary scenario, capable of combining, integrating and solving the research issues raised by the study of mortars, plasters and pigments (Gliozzo et al. 2021).

The first group of contributions explains how mortars have been made and used through the ages (Arizzi and Cultrone 2021; Ergenç et al. 2021; Lancaster 2021; Vitti 2021). An insight into their production, transport and on-site organization is further provided by DeLaine (2021). Furthermore, several issues concerning the degradation and conservation of mortars and plasters are addressed from

practical and technical standpoints (La Russa and Ruffolo 2021; Caroselli et al. 2021).

The second group of contributions is focused on pigments, starting from a philological essay on terminology (Becker 2021). Three archaeological reviews on prehistoric (Domingo Sanz and Chieli 2021), Roman (Salvadori and Sbrolli 2021) and Mediaeval (Murat 2021) wall paintings clarify the archaeological and historical/cultural framework. A series of archaeometric reviews illustrate the state of the art of the studies carried out on Fe-based red, yellow and brown ochres (Mastrotheodoros et al. 2021); Cu-based greens and blues (Švarcová et al. 2021), As-based yellows and reds (Gliozzo and Burgio 2021); Pb-based whites, reds, yellows and oranges (Gliozzo and Ionescu 2021); Hg-based red and white (Gliozzo 2021) and organic pigments (Aceto 2021). An overview of the use of inks, pigments and dyes in manuscripts, their scientific examination and analysis protocol (Burgio 2021) as well as an overview of glass-based pigments (this paper) are also presented. Furthermore, two papers on cosmetic (Pérez Arantegui 2021) and bioactive (antibacterial) pigments (Knapp et al. 2021) provide insights into the variety and different uses of these materials.

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Introduction

Potential connections among several fields in the technological processes linked with the manufacture of different types of materials and products represent an intriguing research opportunity. The study of ancient innovation and technological change is of paramount importance in archaeomaterial research (Erb-Satullo 2020). Essential for such technical implementation was the ability to control fire and heat. The controlled heating process and, more in general, the development of pyrotechnology and the use of high temperatures made the connection between glass technology, metallurgy and vitreous materials and pigments possible (Brøns 2019; Fenn 2015).

Glassmaking can be dated back to 2500 BCE in Mesopotamia and the most important technological application was the production of artificial stones, including lapis lazuli (Beretta 2009). The large-scale production of glass in both Mesopotamia and Egypt can be dated to around 1500 BCE, and the material and technology spread from Syria (Shortland, 2004).

During the New Kingdom period in ancient Egypt (c. 1550–1069 BC), the manufacture of glass, faience and synthetic pigments was probably carried out in the same workshop (Hodgkinson 2019). Chemical and isotopic analysis of glass indicates that diverse glassmaking centres were active in Mesopotamia and Egypt (Erb-Satullo 2020 and references contained therein).

Fire is not the only common denominator in these manufacturing processes, as a wide variety of mining activities are connected with natural and artificial pigment production. The mining of copper can be related to the procurement of azurite and malachite (Brøns 2019); in addition, copper is also used for the preparation of Egyptian blue.

The preparation of artificial “cobalt”-blue may be considered the earliest example of dark glass produced for the imitation of natural stone lapis lazuli and azurite; the green frits were manufactured for the imitation of semiprecious stones such as turquoise and other green gemstones (Fenn 2015). The correlation between faience and glass also suggests that they were part of the same (artificial) stoneworking province in Egypt (Nicholson 2012).

Smalt pigment shares many common aspects with *giallorino*, related to glass technology. Both glassy pigments were introduced almost in the same period of time: smalt most probably as a substitute for costly natural ultramarine and azurite and *giallorino* as a substitute for orpiment, a toxic pigment composed of arsenic sulphide.

The production of glass and pigments is recorded at the San Giusto convent in Florence. Finally, it is worthy of note that in the sixteenth-century treatises written by Bernard Palissy, Giambattista Della Porta and Ferrante

Imperato, the description of *giallorino* is linked with the smalts used in goldsmith and ceramic production (Seccaroni 2006).

The objective of this manuscript is to give an overview of the possible uses of glass-based colouring materials through the discussion of the particular characteristics of blue smalt and lead–tin yellow type II and their use in painting. General features, terminological issues and history of use of these pigments will be addressed through the analytical evidence gathered by the authors in several sites in Italy and Southern Switzerland. In addition, considerations regarding the analytical protocol and the alteration and degradation processes of such pigments will be included and a critical discussion on raw material procurement proposed.

Smalt

Chemical composition

Smalt is a blue potash glass pigment where the blue colour is due to the presence of cobalt (Zlámálová Cílová et al. 2020; Berrie 2012; Mühlethaler and Thissen 1993).

The elemental chemical composition of this pigment is variable as the main components may vary in the following minimum and maximum values: SiO₂ (65–72%); K₂O (10–21%); CoO (2–18%). The presence of elements as impurities due to the raw materials used for the manufacturing process of the pigment (Ba, Ca, Na, Mg, Ni, Fe, Cu, Mn, Bi) does not allow a precise chemical formula to be proposed (Mühlethaler and Thissen 1993).

Manufacturing process

The cobalt mineral used for smalt production in Europe during the Middle Ages was smaltite (Co, Ni)As₃₋₂, mineral of the series skutterudite. Erythrite (Co, Ni)₃(AsO₄)₂·8H₂O and cobaltite (Co, Fe)AsS were CoO sources during the seventeenth and eighteenth centuries (Mühlethaler and Thissen 1993). Recipes and technological processes of smalt production can be found in treatises dated from the sixteenth century (Salerno and Ferroni, 1999; Santopadre and Verita, 2006; Borgia and Seccaroni, 2007).

In the manufacturing process, the cobalt oxide, derived from the roasting of cobalt ores, was melted with silica and potash or added to molten glass. After pouring in cold water, the glass shattered into particles ready to be ground and elutriated (Altavilla and Ciliberto, 2004).

The pigment was available in different grades from pale grey to deep blue, with the colour being dependent on the cobalt content and particle size (Mühlethaler and Thissen 1993). To this basic recipe, variation in the content of the

major and/or minor elements can be diagnostic for particular artists or for characteristic painting techniques. For example, in Rembrandt's paintings, two different types of smalt were differentiated on the basis of NiO:CoO ratio (Janssens et al. 2016).

Nomenclature

Various terms have been ambiguously used indicating the blue colour. As reported by Seccaroni and Haldi (2016), Pliny the Elder used the word *sappirus* for lapis lazuli but also for vitreous materials, *cyanus* for Egyptian blue and *caeruleus* for the colour and the pigment used in wall paintings.

The terms *smalto* and *smaltino* found in early Italian literature should not automatically be associated with smalt; these terms might refer to a vitrified pigment—as described by Vitruvius—composed of sand, copper and potassium nitrate (Merrifield 1849).

Another important term generating confusion is *zaffre* or *zaffera* or equivalent words. Merrifield (1849) states that the pigment *smalto di Flandra* (“Flanders smalt”) made in Venice corresponded to zaffre and that its composition was “very close to the pigment we now call smalt”. According to Fay (1920) and Tingry (1804), zaffre is an impure cobalt oxide obtained after the roasting process of the Co-bearing raw material with sulphur and arsenic driven off. In more recent studies (Zlámalová Cílová et al. 2020; Molera et al., 2021), it is reported that it is the result of cobalt ores roasting at temperatures up to 700 °C, also mixed with siliceous sands. When zaffre was melted with potash and sand, blue smalt was produced; the violet variety was obtained by adding soda instead of potash (Mühlethaler and Thissen 1993). Based on these references, zaffre may be considered the basic product for the manufacturing of smalt pigment.

Whilst “smalt” commonly refers to the blue cobalt-based pigment, other colours also appear to have been marketed under the same name, notably greens, reds, violets and yellows (as in “smalt green”, etc.). These were presumably glass, but opacified with different compounds (Eastaugh et al. 2013; Kunckel 1689).

Appearance and use

The earliest use of blue smalt in wall paintings was found in Khara Khoto in central Asia and in the monastery of Chora, Constantinople (1325–1453 C.E.). In Europe, this pigment was found in fifteenth-century wall paintings (Delamare 2008).

Blue smalt was a valid alternative to other blue and costly pigments such as azurite and natural ultramarine for the possibility to be used in lime-based wall painting techniques for its (apparent) compatibility with lime, also mixed with other pigments.

In easel painting, smalt was very common in fifteenth–sixteenth-century Flemish paintings. The smalt pigment was frequently used in Rembrandt's studio, as seen in the Saul and David painting (c. 1652; Janssens et al. 2016). Smalt has been also used in Southern American Colonial paintings (fifteenth–sixteenth century), most probably imported from Europe through Spanish dealers (Seldes et al. 1999). Its use became common in Europe in the sixteenth century (Bersani et al. 2014). In the “Epirus school” of (wall) paintings (NW Greece) executed in 1531/2 in the Filanthropinon monastery and in later paintings dated 1542 and 1560, respectively in the narthex and exonarthex walls, particular smalt composition was detected. In fact, the chemical composition of the pigment is different from the common products due to the high sodium content vs potassium, the low concentration of Co and the presence of manganese necessary for balancing iron content in the glass structure (Mastrotheodoros et al. 2019).

Smalt has been widely used in wall paintings in aqueous media and lime; it has been used in oil media, also with the addition of white lead to prevent discoloration processes (Mühlethaler and Thissen 1993).

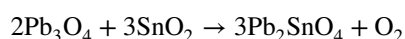
Smalt was used not only as pigment but also for other specific applications. Mixed with other pigments including lakes has been found in Rembrandt's mid-seventeenth century easel painting for its drying properties and to give texture and transparency to the paint (van Loon et al. 2017). Smalt was recommended in the eighteenth century as a siccativ for poor-drying blue pigments (Palomino y Velasco 1715). Furthermore, the intentional addition of colourless glass powder and silica in paint and preparation layers can be dated back to the first decades of the fifteenth century in the Netherlands and Germany and remained a practice until the seventeenth century (Lutzenberger et al. 2010), though the role of glass as drying agent is still debated (Berrie 2012).

Lead–tin yellows (types I and II)

Chemical composition

There are two types of lead–tin yellow pigments: type I with chemical composition Pb_2SnO_4 (orthorhombic form) and type II containing free Sn-oxide and silicon with corresponding chemical formula $PbSnO_3$ or $Pb(Sn, Si)O_3$ (Kühn 1993). The cubic form of the lead stannate $PbSnO_3$ is responsible for the opaque yellow of the glasses (Tite et al. 2008).

Lead–tin yellow type I was produced by burning at $T = 800–900$ °C minium (Pb_3O_4) and cassiterite (SnO_2) according to the following reaction



At lower temperatures, a residue of Pb_3O_4 remains, and at higher, PbO and SnO_2 can be found deriving from the decomposition of Pb_2SnO_4 (Šefců et al. 2015).

Lead–tin yellow type II was traditionally produced for calcination of lead–tin yellow type I or roasting Pb , Sn and Si oxides with 2:1:1 molar ratio, at $T = 850^\circ\text{C}$, according to the following reaction



where $[3\text{PbO} - 2\text{SiO}_2]$ is a colourless glassy phase and $[\text{PbSn}_{1-x}\text{Si}_x\text{O}_3]$ is the yellow pigment. During this process, Pb_2SnO_4 incorporates variable amounts of silica which is substituted for SnO_2 (Matin et al. 2018).

Manufacturing process

A critical review of historical sources from the fourteenth–fifteenth centuries concerning *giallorino* is reported in Seccaroni (2006). In particular, the old recipes reported in the *Manoscritto Bolognese* (Guerrini and Ricci 1887) and *Il libro dell'arte* by Cennino Cennini (Frezzato 2008) are discussed, taking into consideration the method of production, the use with other pigments and the physical properties.

Tite et al. (2008, and references contained therein) report an early fifteenth-century recipe for the production of lead–tin yellow for glasses where a two-stage process is mentioned. The first step produced the lead–tin *calx* obtained by melting and burning one part of lead metal and two parts of tin metal. The second step produced the lead–tin yellow *anime* mixing and then remelting four parts of *calx*, five parts of minium (Pb_3O_4) and one part of silica. The final product has the chemical composition of the cubic form of the lead–tin stannate. Therefore, the *calx* was the main ingredient for the production of yellow (and white) opaque glasses (Matin 2019).

Depending on variations in the stoichiometry of the reagents, several products can be formed and the final pigment may have different hues. A moderate rise of silica determines the reduction of the colour strength whilst a milky white product is formed when silica markedly exceeds. When there is a deficit in silica, a mixture of Pb_2SnO_4 and Pb_2SnO_3 is formed, and a (not well defined) glassy phase (Hradil et al. 2007).

Nomenclature

The connection between glass and ceramic technology with the production of *giallorino* is significant. In this context, the term *giallorino* refers to lead–tin yellow pigments as reported in Kühn (1993) even if the term may include other artificial yellow Pb -based pigments as in Seccaroni (2006). In fact, the terms used in the fifteenth and sixteenth centuries

for the designation of *giallorino* contain a direct reference to the production features (*giallorino di fornace o dei vasai*; “*giallorino* of the furnace” or “potter’s yellow”) or indirect evidence to the production sites of Venice and Murano.

Appearance and use

There is evidence of lead–tin yellow type II in several Tuscan panel paintings of the fourteenth century; its use is also reported for an artwork executed by Meliore di Jacopo (thirteenth century) and on the wall paintings in the cathedral of Angers (1270–1280). The earliest evidence of lead–tin yellow type II used in Italian wall paintings is the chapel Bardi di Vernio in Santa Croce in Florence painted by Maso di Banco around 1340; another noteworthy example is its use in the fourteenth-century frescoes in the Abbazia di Chiaravalle Milanese (Seccaroni 2006).

In the seventeenth century, lead–tin yellows, yellow ochre and yellow lake were the dominant pigments in Northern European easel paintings (van Loon et al. 2017, and herein references).

Best practice guide and analytical protocol

When planning a diagnostic campaign for studying paintings, the minimum invasiveness and maximum representativeness of the data collected is pursued. The sequence of data collection must lead to the acquisition of information aimed at answering the research questions under investigation. Therefore, the analytical protocol must be congruent with the objectives of the study.

There is no single protocol for studying glass-based pigments. Instead, there is a logical approach involving, firstly, the transdisciplinary study of the object (van Den Besselaar and Heimeriks 2001; Leona and Van Duyne 2009; Heritage and Golfomitsou 2015) and, secondly, the subsequent design of further investigations. This applies not only to the study of paintings or glass-based pigments, but also to any other cultural artefact.

An extensive, up-to-date and fruitful discussion of analytical protocols to be implemented in a painting pigment study program, as well as the application of conventional and unconventional analytical techniques (their potential and limitations), is reported in Coccato (2017) and references therein.

As glass-based pigments have been used in various fields of pre-industrial and industrial production, it is difficult to operate within strict guidelines. In the field of painting, if the aim of the investigation is to recognize the pigments present in an artefact, it is possible to operate with conventional methodologies, limiting the diagnostic field to mapping the painting using multispectral imaging techniques

(Lotti 1999). In the case of smalt, Cosentino (2014) shows a flowchart for the identification of blue pigments using multispectral imaging: blue smalt appears bright in UV imaging, dark in IR imaging (Fig. 1b) and with red colours in infrared false colour (Fig. 1c). The hand-held X-ray spectrometry (HH-XRF) associated with visible reflected spectroscopy (Vis-RS) is the most suitable “in situ” non-invasive point techniques for the identification of blue smalt (Galli et al. 2006; Bonizzoni et al. 2008; Poldi 2009). The presence of Co (and \pm As) associated with K, also including Si (if detectable; HH-XRF) and the detection of absorption bands at 530, 590–600 and 640 nm, and relative maxima at 460, 560 and 620–630 nm (Vis-RS) are diagnostic for the original pigment. This is true when the pigment is well preserved (Poldi 2009; Cosentino 2014); on the contrary, when the pigment is highly altered or used in mixture with other pigments or present in complex stratigraphies, the recognition can be difficult (Poldi 2009) and a micro-sample is required. The use of HH-XRF can also be used to detect yellow glass as the presence of Si, Pb and Sn is characteristic for this pigment. The use of X-ray diffraction (XRD) and Raman spectroscopy can be an ancillary analytical technique for the detection of lead–tin yellow type II (Hradil et al. 2007). Glass-based pigments are easily recognizable under polarized light microscopy (PLM), in thin and cross section (stratigraphy): the shape of the grains is always angular and they do not show any birefringence. The state of conservation can also be documented by studying the micro-textures of the individual grains with scanning electron microscopy coupled with microanalysis (SEM/EDX). The combination of PLM and SEM/EDX allows for the in-depth analysis of the multi-layered sequence and the painting technique (Regazzoni et al. 2018). These aspects are discussed extensively in the following section. A micro-invasive approach is necessary when questions such as processing techniques, pigment manufacture and the provenance of raw materials are addressed. In the case of glass-based pigments, defects (micro-textures) are rare, but the chemical and geochemical

composition can provide important clues for the reconstruction of technological history.

The comparison of data obtained with different analytical techniques must be taken into adequate account because of the different volumes investigated.

Case studies: glass-based pigments in paintings and alteration processes

Smalt blue

Despite the wide use in wall paintings and its apparent stability, smalt may discolour turning light grey, as documented in many case studies and experimental replicas (Manship 2017). Like all glass, it is sensitive to water and moisture. In painting, glass-based pigments are more stable in wall paintings (*secco* or *fresco* technique; Mühlethaler and Thissen 1993; Boon et al. 2001; Gil et al. 2011) and less stable in oil and egg tempera (Coccatto et al. 2017).

The degradation process is undoubtedly a complex one, and the variables involved depend on the textural (grain size and grain boundary surface), compositional features of the pigment, stability of the binder (lime, oil, tempera) and the microclimate in which the painting was stored (P, T and moisture). An updated reference list can be found in Manship et al. (2021) and Coccatto et al. (2017).

Case studies from Switzerland and Italy analyzed by the authors as preliminary research for conservation works were included for presenting the most important features of the pigment and degradation processes.

The most typical visible alteration of smalt blue is the colour change (Manship et al. 2021 and references therein; Coccatto et al. 2017 and references therein). Figure 2 reports the use of blue smalt pigment for the decoration of the blue drape of the figure in the painted vault executed between 1628 and 1630 in the lateral Rosario chapel built by the von Roll family in the St. Francesco Church at Locarno (Tessin,

Fig. 1 Mei’s painting “Il ciarlantano” – “The swindler,” 1656, oil on canvas. **a** Easel painting under visible (Vis) light; **b** same painting under infrared (IR) light; **c** same painting in infrared false colour

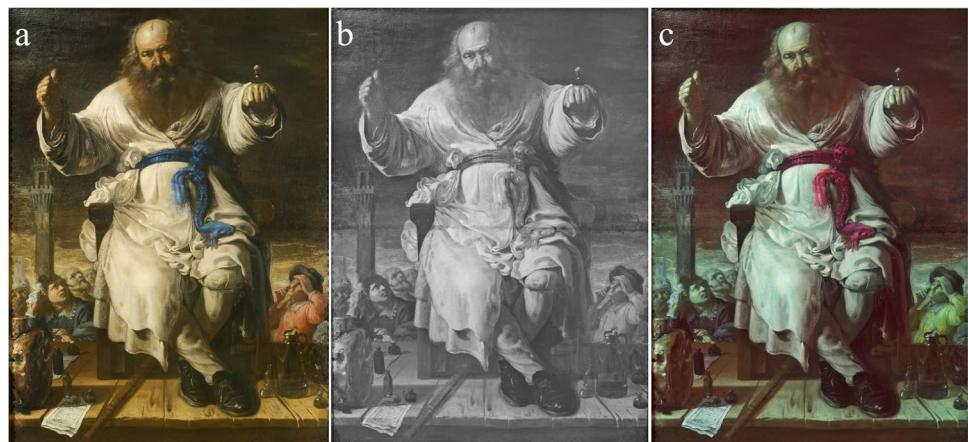
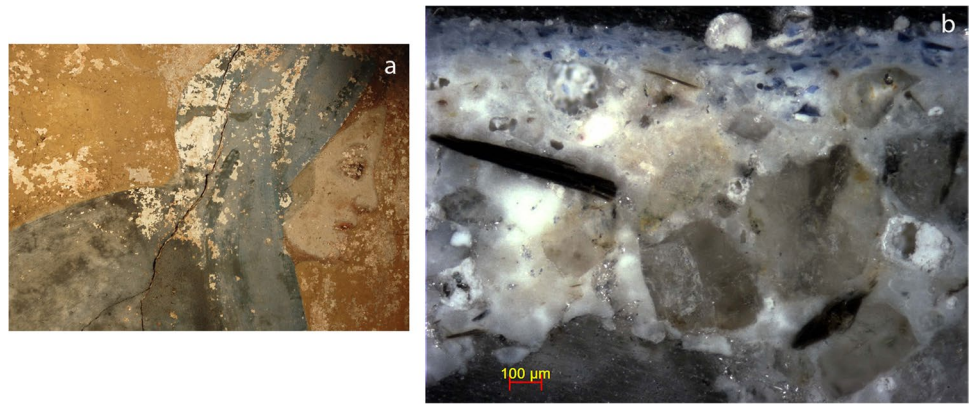


Fig. 2 Rosario Chapel, St. Francesco Church, Locarno (Tessin Switzerland). **a** Blue drape executed using smalt. **b** Cross section of the blue drape collected from the back of the figure (Vis incident light)



Switzerland). This chapel displays stucco decorations and wall paintings made by unknown artists or studios. The blue decoration (Fig. 2a) shows evident alteration processes of the original tone of the pigment that can be also found in the cross section (Fig. 2b) where the individual angular smalt grains mixed with lime and applied directly on the ground layer (*intonaco*) exhibit different intensities of the blue colour.

This colour variation caused by the change of the structural coordination of Co^{2+} as a consequence of K depletion (Gil et al. 2011; Cianchetta et al. 2012; Robinet et al. 2013; Coccato et al. 2017) is manifested by the formation of characteristic coronitic micro-textures. To demonstrate these features, SEM/EDX analyses were carried out on samples collected from the wall painting representing the *Madonna and Child with Saint Rocco and Saint Sebastian* that dates from the 1530s executed by an unknown painter in the St. Rocco Oratory (sixteenth century) in Tessin Canton (Switzerland). In these samples, pigment degradation is manifested by the formation of coronitic micro-textures that initiate along grain boundaries, at the interface between pigment and binder, and proceed towards the center of the pigment grain (Fig. 3). The coronitic micro-textures maintain the original shape of the grain. In this situation, the process that develops is leaching. When the coronitic micro-textures are affected by micro-fractures, the contours of the pigment grains become irregular, the degradation process is at a more advanced stage of transformation and corrosion occurs, as also reported in the literature (Manship et al. 2021; Plesters 1969; Santopadre and Verita, 2006; Giovanoli and Mühlethaler 1970).

Compositional variations detected through electron micro-probe analysis (EMPA) are reported in the diagrams of Fig. 4. Here, data obtained by the authors (from the aforementioned St. Rocco Oratory) were compared with those from literature in Italian contexts in Rome (Church of Sant'Eligio degli Orefici and Serra Chapel, Church of San Giacomo degli Spagnoli, sixteenth century; Santopadre and Verita 2006). All the reported examples

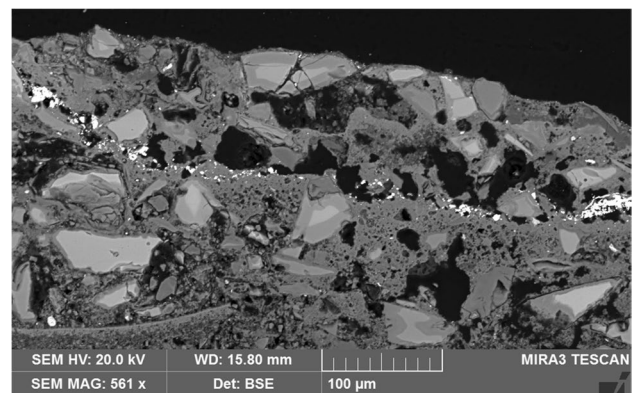
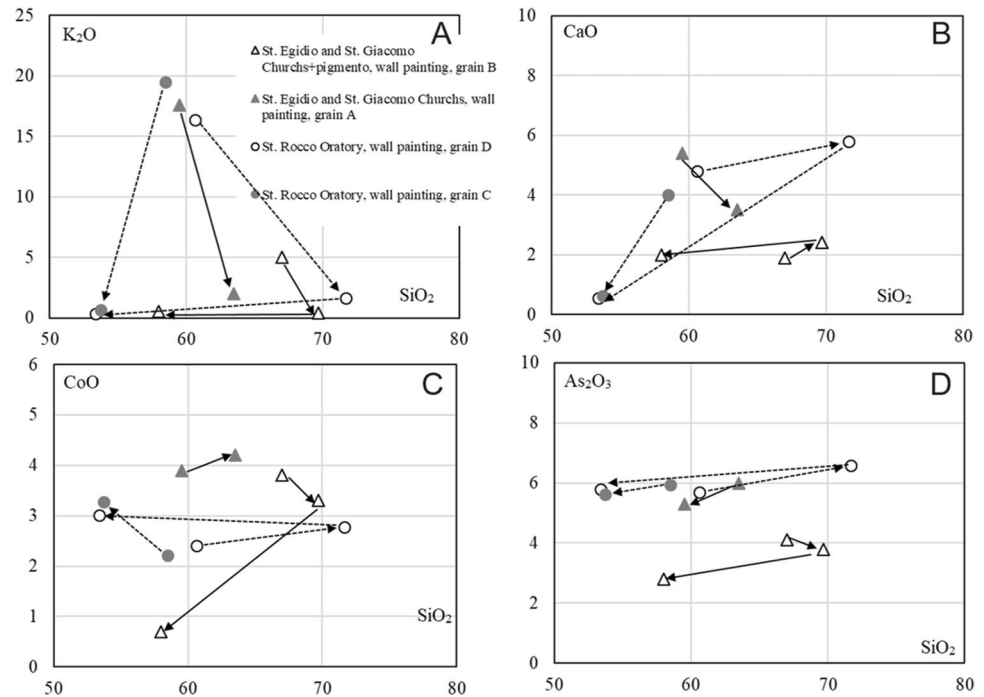


Fig. 3 St. Rocco Oratory, Ponte Capriasca, Tessin, Switzerland. In the BSE image, the coronitic structures present around the pigment grains are clearly evident. Some of the grains show convoluted edges and forms of corrosion

show very similar trends as the rims of the smalt grains are markedly depleted in K_2O with respect to the well-preserved core (Fig. 4a). Small changes were observed for CoO and CaO contents (Fig. 4b–c). When corrosion is present, there is also a depletion of SiO_2 content (Fig. 4, grains indicated with B and D). These chemical changes show that the discolouration is not caused by the loss of cobalt (Giovanoli and Mühlethaler 1970; Boon et al. 2001), but to the leaching of potassium. The presence of the coronitic phases conditions the progress of the process. When the coronitic micro-textures is continuous and well developed, it slows down the diffusion and exchange between the grain and the binder, and leaching is slowed down (Verità et al. 2000; Santopadre and Verita, 2006). On the other hand, when the corrosion processes start, the coronitic layer is not continuous and this facilitates the removal of network modifier ions; silicates redeposit as silica gels (Santopadre and Verita 2006). The corrosion mechanism is strongly affected by pH values (Ahmed and Youssof 1997; Vilarigues and Da Silva 2009; Machado and Vilarigues 2018).

Fig. 4 Binary diagrams of chemical compositional of blue small grain pigments. **a** SiO_2 vs K_2O ; **b** SiO_2 vs CaO ; **c** SiO_2 vs CoO ; **d** SiO_2 vs As_2O_3 (the grains A and B refer to the paper Santopadre and Verita 2006)



There is no full agreement on the mechanisms governing the alteration and degradation of glass-based blue pigment as indicated from the referenced literature. However, it is clear that multiple processes contribute to the degradation of this glass-based blue pigment.

Both the structure and composition of the glass and the action of external variables such as environmental parameters, as well as the nature of the binder and the painting technique, may play important roles (Coccatto 2017; Coccatto et al. 2017, and references therein).

Lead–tin yellow (type II)

The study of the painting materials in the Late Gothic Chapel of St. Marta Church in Carona (Tessin, Switzerland) offers an interesting example of yellow lead–tin type II pigment alteration. In particular, samples from the wall paintings of the Eastern façade executed around 1486 by Cristoforo da

Seregno were collected with the aim of understanding the uneven and inconsistent darkening of the painted surfaces (Fig. 5).

The observation under an optical microscope indicates the presence of the pale yellow pictorial layer composed of a glassy pigment with different hues ranging from yellowish to white–grey mixed with lime. The paint layer is over a lime-based preparation layer (Fig. 6a). Microchemical analysis carried out on the (unaltered) yellow paint layer of St. Francesco's halo (Fig. 6c) confirms the variability of the chemical composition of the pigment *giallo di vetro* (lead–tin yellow type II). In fact, one pigment grain has the chemical composition reflecting that of the cubic form of lead–tin stannate (Fig. 6c) whilst another grain contains only Pb and Si (Fig. 6d), thus reflecting the variable amount of the chemical constituents as mentioned by Hradil et al. (2007).

Preliminary observations concerning the alteration processes affecting lead–tin yellow pigments indicate

Fig. 5 Late Gothic wall paintings (St. Marta Church, Carona, Switzerland). **a** The halos of St. Francesco and Christ are almost completely darkened due to alteration processes affecting Pb–Sn pigments used. In the lower part of the halo of the Saint, the original yellow pigment is unaltered in a limited area. **b** Detail of the previous picture



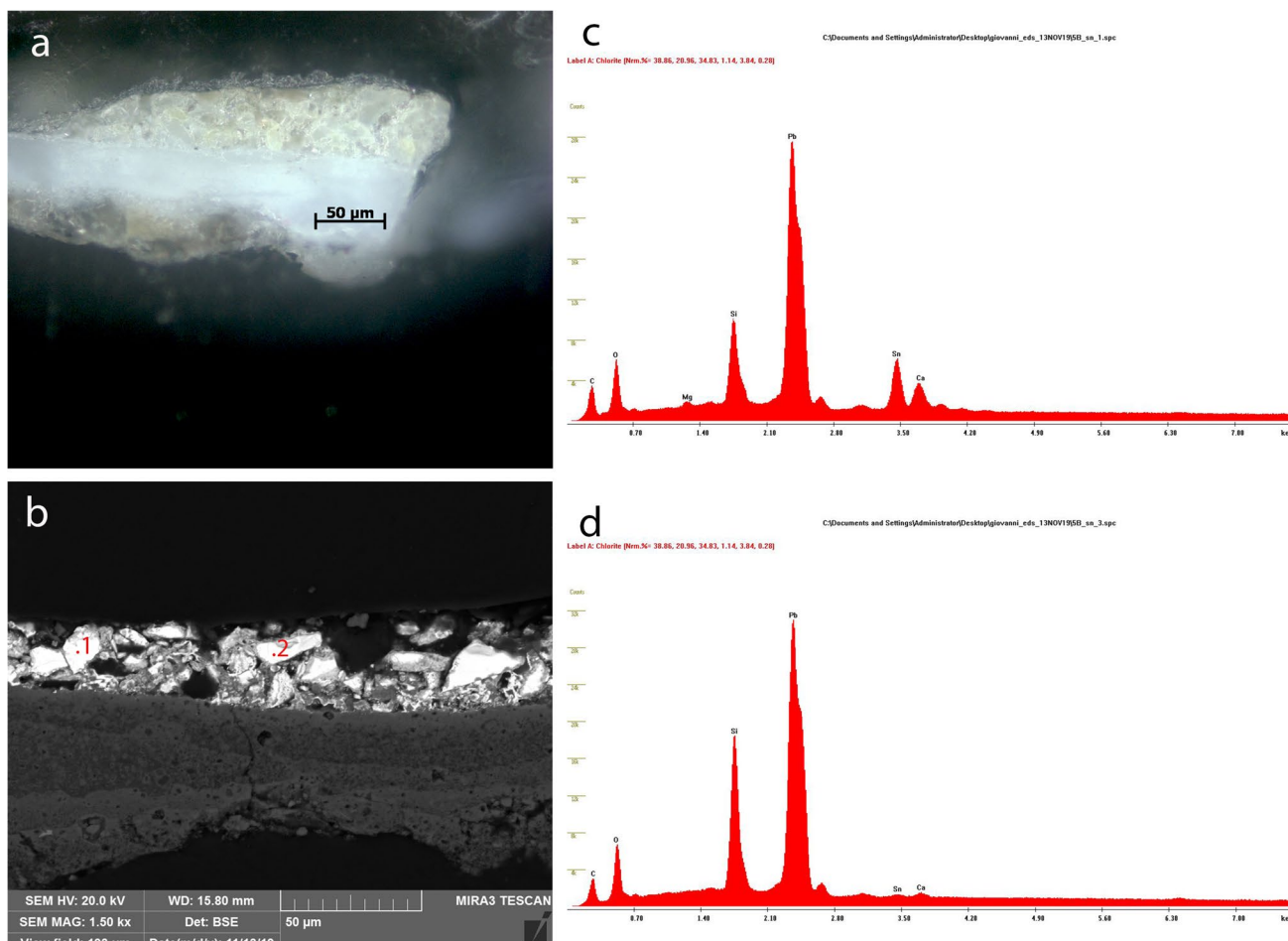


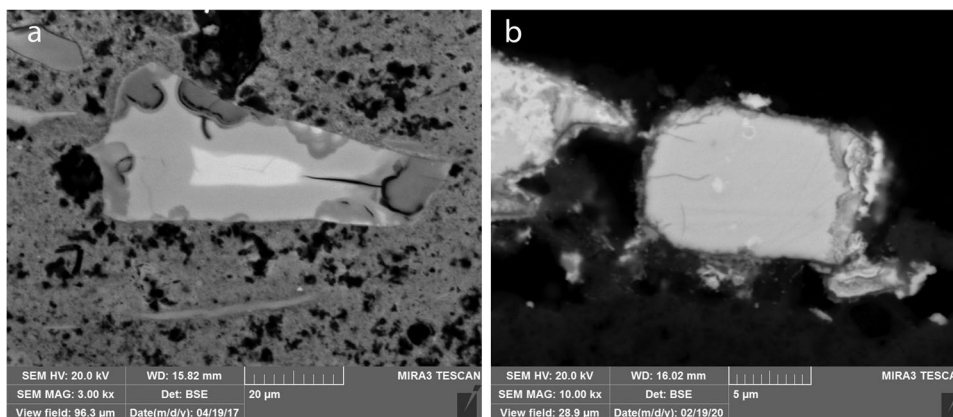
Fig. 6 Microscopic examination of the unaltered yellow pigment from the halo of St. Francesco. **a** Micro-stratigraphic sequence under incident Vis light. **b** BSE picture indicating the grains (1 and 2) analyzed through EDX. **c–d** Chemical composition respectively of

the grains 1 and 2 (**b**). Microchemical analysis reported in **d** shows a depletion of Sn and Si enrichment compared with microchemical analysis reported in **c**

microstructural features very similar to those observed for blue smalt pigment. In fact, in comparing the grains of the two pigments, it is possible to observe that, except for the coronitic micro-texture clearly visible for the blue smalt

pigment (Fig. 7), leaching areas, detaching of flakes and micro-cracks formations are common features. The formation of micro-cracks like those visible in the right side of the blue smalt grain (Fig. 7a) is a consequence of the

Fig. 7 Micro-textural features of glass-based pigments (BSE images). **a** Smalt grain in the seventeenth-century wall painting (St. Rocco Oratory, Ponte Capriasca, Tessin, Switzerland). **b** Pb–Sn yellow pigment type II in the sixteenth-century wall painting (St. Marta Church, Tessin, Switzerland)



density modification of the glass structure due to potassium leaching determining an increase of silica concentration. Another consequence is the formation of micro-flakes prone to detaching. The yellow glass pigment (Fig. 7b) exhibits a heterogeneous composition as the grain is primarily composed of Si and Pb, suggesting the presence of a colourless PbO-SiO₂ phase (Hradil et al. 2007). This phase is enriched in silica (compared to the stoichiometry of the pigment) and leads to a drastic reduction of the density with the formation of micro-cracks visible on the left side of the grain. The bright spot visible in the middle of the grain is composed of Pb, Si and Sn, and represents the only zone of the grain having a chemical composition corresponding to lead–tin yellow type II. The right side of the grain clearly exhibits incipient and detached micro-flakes composed only of Pb. The complex variability of the chemical composition makes it difficult to understand if the elemental distribution is a consequence of or responsible for the decay that has occurred. In fact, we cannot exclude the leaching of Pb-oxide from the glass structure (Heck et al. 2003).

The darkening of the painted surfaces (Fig. 5a) is due to the formation of plattnerite (β -PbO₂) as detected through X-ray diffraction executed on a small flake collected from the painted surfaces (data not reported here). Its formation may be due to incorrect preparation of the pigment obtained with an excess of silica. The addition of Sn in adequate proportion (at least 5 wt%) was of paramount importance as it inhibited totally or partially the instability to the light of Pb-based pigments and the consequent formation of plattnerite. The presence of plattnerite correlated with lead–tin yellow type II deserves more accurate research. In another case study (Costantini et al. 2020), the darkening associated with this glass pigment was explained as the total transformation of white lead mixed with lead–tin yellow type II even if no traces of the original white pigment have been detected. Microstructural and microchemical analysis are still in progress to understand more in depth the role that the production technology of this pigment can play in the darkening process of the painted surfaces.

Tracing of pigments

The postulate that defines what is the limit for an unambiguous identification of the supply source of raw materials has been formulated by Weigand et al. (1977): “It is possible to recognize the source of raw materials if the chemical or mineralogical differences between different natural sources are greater than they are within each source”.

There is a direct correlation between the composition of the artefact and that of the raw material source when the natural (geological) material is used without any treatment. This is the case when the glass of volcanic origin is

used in wall painting (Piovesan et al. 2011). Most glass-based pigments are produced using a mixture of natural raw materials, so no conclusions can be drawn about their origin without taking into account the entire cycle of production.

However, provenance studies of blue glass pigment use some minor or trace chemical elements linked to cobalt.

Starting in the fifteenth century, there are four geochemical groups that have been identified, and all of them can be traced to mines in Central Europe (Delamare 2008):

1. Co-Zn-In-Fe association (twelfth to fifteenth century): Erzgebirge, probably Freiberg mine;
2. Co-Ni-Mo-Fe association (fifteenth century): Schneeberg region, for roasting skutterudite (Schneeberg I)
3. Co-As-Ni-Bi-W-Mo-U-Fe association (sixteenth to eighteenth century): from the Schneeberg region, but obtained by a different mineral process (Schneeberg II)
4. Co-Ni-As association (from the nineteenth century): the origin is not identified, but the sources of supply can still be identified in the region of Saxony.

One topic that deserves particular attention in terms of research is that related to the origin of raw materials, in particular the relationships between geological material and products and/or by-products that are formed during production. An additional complication arises from the fact that raw materials used in the past may no longer be available today. The minerals that we find today in the dumps of ancient mines are the waste products of the exploitation and certainly not the useful mineral, which is obviously no longer present today (Tizzoni 2020). Therefore, provenance studies should be based on statistical evidence rather than direct correlations with the geochemistry of the sources and then compared with the geochemistry of the artefacts (or semi-finished products).

If we consider smalt, as an example, it is the product of a long and complex chain of technological operations not necessarily carried out in a single place (Zlámálová Cílová et al. 2020). Figure 8 shows the process schematically. As reported earlier, the first step is the production of the zaffre; the second is the addition and melting of sand and a potash flux (Mühlethaler and Thissen 1993; Zlámálová Cílová et al. 2020).

The last known part of this process is the extraction and production of chromophore cobalt.

Zaffre and blue smalt production is well studied, and recent archaeometric papers have outlined the main actions that define the *chaîne opératoire* (Delamare 2008; Santopadre and Verita 2006; Gratuze 2013; Mimoso 2015; Zlámálová Cílová et al. 2020). A multidisciplinary study defined the principal chemical association as useful for provenance studies in

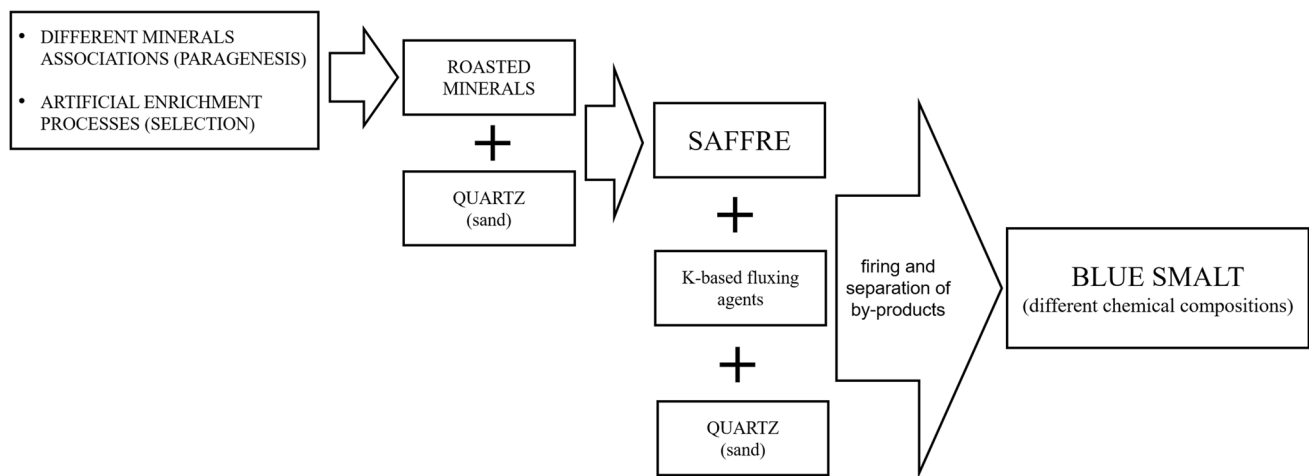


Fig. 8 Schematic diagram indicating the production of smalt blue

Western Europe and Mediterranean regions (Delamare 2008; Gratuze 2013).

If we consider yellow glass-based pigments, the provenance of lead pigments through the determination of lead isotope ratios is a possible analytical procedure (e.g. Brill et al. 1997; Fortunato et al. 2005; Sotiropoulou et al. 2010; Nord et al. 2015). It yielded good results even in the case of Flemish paintings from the early modern period, when pigments were generally traded over long distances (Fabian and Fortunato 2010). The situation is more complicated when we consider the tin supply sources. Studies on the mines that supplied this metal mainly refer to three important mining sites: the tin deposits of Cornwall and Devon, the Saxon-Bohemian Metalliferous Mountains and the Iberian Peninsula (Nessel et al. 2018). Using tin-isotopic ratios from tin sources in southern England and the Saxon-Bohemian Ore Mountains, they vary widely and often show data overlapping. This sometimes makes it impossible to establish unambiguous traceability between artefact and mining area (Nessel et al. 2018).

Concluding remarks

Glass-based pigments represent a particular aspect of artistic production because they bring together pre-industrial know-how from different fields and highlight the links that existed in the past between different productions. The recycling of waste and by-products was probably very active in the past, so much so that metallurgical waste may represent an excellent semi-finished product for glass colouring or perhaps already to produce a useful material for the colour market.

Among the glass-based pigments described in technical manuscripts and found in pictorial artefacts, smalt blue

and lead–tin yellow type II play an important role because, along with Egyptian blue, they derive from a manufacturing process. Hence, the extensive scientific interest is devoted to the study and preservation of these pigments.

The structure of these pigments is that of a non-crystalline material and from this derives both the methodological approach and the analytical techniques used for their identification, study of production technology and preservation protocols.

“In situ” identification of a glass-based pigment is relatively simple: the use of an optical system allows for the recognition of the uneven form of the morphology and their homogeneity. Like glass, however, these pigments are not very stable when used, and degradation processes lead to their rapid deterioration, perhaps as early as the first phase of their application.

The variability of the chemical composition of the raw materials, the technological process and the available recipes, the chronological and geographic contexts, the painting technique, past restoration treatments, the exposure to environmental variables primarily correlated with water and vapour supply, are all factors that may condition the stability of glass-based pigments. Understanding the interconnections of these aspects is crucial when approaching the study of glass-based pigments both in terms of preliminary characterization for their identification and for more in-depth research (reconstruction of the *chaîne opératoire*). The proposed case studies demonstrated as the micro-scale analytical approach (micro-texture) reveal important data complementary to bulk analysis.

Experimental works based on the replication of the original painted surfaces may help in formulating a better understanding of the mechanisms governing their stability vs instability under different conditions.

Another field that deserves particular attention in terms of research is tied to the provenance of raw materials, particularly in terms of cobalt mines.

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