Journal of Cultural Heritage 66 (2024) 166–186

Contents lists available at ScienceDirect

Journal of Cultural Heritage

journal homepage: www.elsevier.com/locate/culher

Review

The fresco wall painting techniques in the Mediterranean area from Antiquity to the present: A review

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ARTICLE INFO

Article history:
Received 10 July 2023
Accepted 20 November 2023

Keywords:
Wall painting
Fresco technique
Lime mortar
Pigment
Compatibility
Conservation of architectural heritage

ABSTRACT

Fresco wall paintings are one of the oldest artforms in our cultural heritage, dating back to the second millennium BC. In this work, we carry out a thorough review on the evolution of the fresco wall painting technique from Antiquity to the present day. Focused on the Mediterranean area, the aim is to gather in-depth information on different technological aspects of this decorative artform such as execution procedure, materials used and pictorial palette. Considering that the recognition of the pictorial technique (*a fresco*, *a secco*, or *a mezzo fresco*) is often difficult since the identification of organic binders can be a challenging issue, the assignment of well-known non-alkaline-resistant pigments to the fresco technique might not always be precise. With this in mind, this review aims to highlight the contradictions found between the bibliographical sources on the fresco technique and recent scientific studies in relation to the preparation of materials, the execution on the wall and the incompatibility of certain pigments with the alkaline environment created by this pictorial technique.

Introduction and research aim

Wall paintings are understood as any kind of pictorial decoration executed on a wall (i.e., cave or masonry), and as such are considered one of the oldest forms of artistic and historical heritage which must be preserved in situ [1]. Apart from their unquestionable aesthetic worth, wall paintings are also of high historical and artistic value in that they act as a historical document that offers insights into the history, architecture, and customs of the time. This explains why in recent decades there has been increasing interest in frescoes within the field of conservation and restoration of architectural heritage.

Over the course of the long history of wall painting, a wide range of different techniques have been used. The first examples were cave paintings dating back to the Upper Palaeolithic Age, and more specifically to the Aurignacian period (30,000 BCE), although this artform reached its zenith during the Magdalenian period around 15,000 BCE e.g., *Altamira* and *Lascaux* caves [2–4]. The first wall paintings associated with buildings appeared later, during the Neolithic (5000 BCE). These were painted on walls covered with blocks of raw earth rendered with mud or clay [5,6]. However, it was not until Antiquity that the first traditional wall paintings appeared: i.e., murals painted on specially prepared surfaces made of traditional mortars, such as lime or gypsum-based ones [7,8]. The walls to which the layers of mortar were applied were made of varied masonry materials, including natural stone and artificial materials such as adobe, rammed earth and fired bricks [5,6].

Before proceeding, we must distinguish between the terms *mortars, stucco* and *plaster* when it comes to wall paintings. The European Standard UNE-EN 16572 (2015) [9] defines the term *mortar* as a material composed of a mixture of one or more binders, aggregates, water, and possible additives used as a bedding, jointing, and surface coatings which subsequently sets and forms a rigid material; *stucco* is more precisely defined as a mortar used for decorative purposes used on facades and building interiors as opposed to *plaster* which is used exclusively in reference to internal coatings. As *stucco* is a broader term, authors will refer to it when describing wall painting mortar coatings. Throughout history and regardless of their specific role in the building, mortars and stuccoes have been mainly composed of: i) a binder, which binds the different components together by means of chemical transforma-

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https://doi.org/10.1016/j.culher.2023.11.018

tions in their composition; ii) one or more aggregates with different grain sizes providing volumetric stability during the drying process and final mechanical strength; iii) (when applicable) additives and admixtures, i.e. materials added to the mortar in small quantities in order to improve existing properties or add new ones; and iv) water, to mix the different components into a fresh mix that can be applied to the masonry [5,10–13]. These components are also found in the mortars used in frescoes. The decoration or artwork was painted onto the last layer of mortar using a range of pigments, defined as a finely ground, coloured powder which is mixed with a binder to create paints that add colour to artworks [14–17].

The binders traditionally used in mortars were clay, lime, and gypsum, although this varied according to the historic period and the geographic area [12]. Lime and gypsum were the most used in ancient times (8000–7000 BCE) in the Middle East, although, it was not until the Greek-Roman period (1000 BCE) that their use spread beyond this region [5,6,8,12]. However, lime was the chosen binder par excellence in the manufacture of mortars in Antiquity (in the Mesopotamian, Egyptian and Mediterranean regions) and in the Middle, Modern and Contemporary Ages until the arrival of Portland Cement in the nineteenth century [18].

As regards the wall painting techniques used, they can roughly be divided into *fresco* (from the Italian word *affresco*, derived from the adjective 'fresh') and *secco* (meaning 'dry'). In the former, the pigments are painted onto the outer layer of mortar (traditionally made with an air-hardening lime of calcitic composition, i.e., *fat lime*) when it is still wet. This enables the pigments to bond to the surface via a carbonation process, i.e., calcium hydroxide reacts with atmospheric CO_2 to form calcium carbonate [19]. In *secco*, by contrast, the pigments are fixed by mixing them with an organic binder and then applied to the dry mortar surface. The mortars are not all lime-based, as mixed (made for example with a mixture of lime and gypsum) or gypsum mortars can also be used. We should also mention other variations such as *mezzo fresco* (*mezzo* meaning 'half' in Italian) in which pigments, previously mixed with lime water, are applied onto a dry mortar, and fixed to the surface by the reactivation of the carbonation process [7,8,20].

In this paper we review the fresco technique, considered one of the oldest forms of painting and therefore of cultural heritage, since it first appeared in the second millennium BC until the present day. To this end, authors will examine the Mediterranean region. This area must be understood not only as the countries surrounded by the Mediterranean Sea but also those territories that make up Western and Eastern Mediterranean, the Adriatic-Ionian region and those countries influenced by the Mediterranean during history (i.e., Switzerland, Macedonia, Bulgaria and Romania) [21,22]. Whilst extensive research has been conducted into wall painting techniques, no specific review has been carried out of the fresco technique. In any case, identifying the pictorial technique (*a fresco, a secco,* or *a mezzo fresco*) often presents problems related to the identification of possible organic binders. In this way, it has been observed that the often-used assignment of some mural paintings to the fresco technique may not always be entirely justified, especially in the presence of unstable pigments (i.e., copper or lead-based). With this in mind, this review aims to:

- Carry out a compilation of the bibliography on fresco wall painting in the Mediterranean area from a historical, technical, archaeological and archaeometric point of view without delving into stylistic aspects. The aim is to gather as much information as possible on this wall painting technique since it first appeared until the present day. To this end, we will be focusing on the traditional sources (painting treatises and art textbooks) which include numerous references to the execution technique and the materials used, comparing them with the archaeological evidence. This will enable us to identify common themes and discrepancies.
- Gather information on the specific materials used in frescoes (binder, aggregates, and pigments) from recent studies, in this way helping to trace the evolution of the fresco over the course of history. In all, the authors will also be looking closely at the differing opinions in the sources and in recent scientific studies regarding the compatibility of certain pigments with the fresco technique.

Evolution of the fresco technique

In this section we examine the development of the fresco technique, as described initially in treatises on architecture and painting and later in art textbooks (Table 1), discussing its evolution in terms of execution procedures and materials and comparing these findings with archaeological evidence. For this purpose, the review has been divided into five historic periods (Prehistory, Classical Antiquity, Middle Ages, Modern Age and Contemporary Age) where the evolution of the fresco technique is discussed throughout time and considering the different civilisations that have existed in the Mediterranean. The fact that some of the different cultures overlap in time, especially during Classical Antiquity (e.g., Greek and Phoenician), implies that a continuous timeline has not always be followed in this review. In view of the numerous contradictions identified regarding the use of pigments in frescoes, Table 2 lists the main pigments referred to in painting treatises and those found through archaeological evidence, with some notes on terminology. When possible, three real examples of the use of each pigment in fresco wall painting has been included, bearing in mind the difficulty in finding examples where 20th century pigments have been used (e.g., Guignet green and titanium white). In addition, it should also be noted that in some of the examples given, analyses that can rule out the presence of organic binders may have not been appropriately carried out. Therefore, the presence of some of the pigments (e.g., copper-based) should be seen with caution.

Prehistory

The use of lime-based mortars dates back to the 8th or 7th millennium BC, when they were widely used in the Near and Middle East [5]. Studies of the wall paintings in the Yarim-Lim Palace (Antakya, Turkey), found that the preliminary drawing was painted while the mortar was still damp, effectively creating what is thought to be the first fresco executed in the Mediterranean area [23,24]. There are also various examples of frescoes during the Bronze Age (3300 – 1200 BCE) [25]. These were used to decorate the walls and the floors of the houses of the elite in the Mediterranean region, and often included scenes depicting power and authority [26]. The oldest surviving frescoes deliberately executed as such, exhibiting a high degree of technical skill [16], date from around the second millennium BC. These examples of Cretan Minoan art can be found in the Palace of *Knossos* (Crete, Greece) [25,27–29] or Pylos (also in Greece) [30,31]. However, it must be considered that intercultural exchanges occurred at the time between the Aegean culture (i.e., Crete, the Cyclades, the Greek mainland south from Thessaly, including the Peloponnese, and Macedonia, Thrace, and western Anatolia) and other Mediterranean territories. For instance, based on stylistic comparisons, the wall paintings of Tell el-Dab'a (Avaris, Egypt) are considered as Minoan-style frescos [32], regarded as a good example of the prevailing style at that time [33]. In relation with the materials used in these thought-to-be frescoes, calcite ($CaCO_3$) appears as the main mineral in the lime plaster, with small amounts of dolomite ($CaMg(CO_3)$) and crushed shell [34,35]. Regarding the pigments

Table 1
Main references and guiding elements in treatises about plaster preparation techniques in the period under consideration.

Historical period	Author/work	Binder	Aggregates	Slaking period	Number of layers	L:S*	
						Arriccio	*Intonaco*
Classical Antiquity (IV BC – I BC)	Pliny the Elder	Lime	Sand; Marble powder	Three years	Five	3 layers – 1:3	2 layers – 1:2
	Marcus Vitruvius	Lime	Coarse sand; Crushed brick; Pozzolans; Marble powder	Three years	Seven	4 layers – 1:3	3 layers – 1:2
Medieval Age (V – XV)	Anonymous, *Mappae Clavícula*	Lime	River sand; Crushed brick; Marble powder	Not mentioned	Not mentioned	1:3 (+ 1/3 crushed brick + 1/6 straw + 2/6 pig fat)	1:2 (+ 1 olive oil + 1 chopped tow)
	Cennino Cennini	Lean Lime	Coarse sand; River sand; Marble powder; Crushed brick	Not mentioned	Three	2 layers - 1:2	1:2
	Leon Batista Alberti	Lime (mixed with gypsum in dry places)	River sand; Crushed brick; Marble powder	>Three months	Three	1 layer Not mentioned	2 layers Not mentioned
Modern Age (XV – XVIII)	Giorgio Vasari	Lime	Marble powder; Pozzolanic sand	Not mentioned	Not mentioned	Not mentioned	1:2
	Andrea Pozzo	Lime	River sand	6–12 months	Two	1:3	1:2
	Antonio Palomino	Lime	Good quality and free-clay sand	4–6 months	Three	Not mentioned	Not mentioned
Contemporary Age (XVIII – present)	Max Doerner	Air-hardening lime	River sand without micas; Marble, limestone and quartz sands	>Two years	Four	2 layers - 1:3	2 layers – 1:2 and 1:1
	James Ward	Air-hardening lime	Gritty sand; Well-washed river sand	One year	Two	1:2	1:3
	Ralph Mayer	Slaked lime paste	Coarse sand; Marble powder	3–6 months	Three	2 layers - 1:3 and 1:2	1:1
	Antoni Pedrola	Air-hardening lime (<5 % MgO)	Coarse and fine quartz aggregate; Marble powder	>Nine months	Two	1:2	1:1
	Josep Minguell Cardenyes	Air-hardening lime	River sand without micas; Marble powder	>Three months	Four	2 layers - 1:3 and 1:4	2 layers - 1:2 and 1:2

L:S*: lime-to-sand ratio according to the number of layers.

Table 2
Main pigments found on fresco paintings in the Mediterranean area. Evidence of their apparent use in the fresco technique are included.

Colour	Pigment	Nature	Pigment composition	Approx. period of use	Evidence
Red	Red ochre; Red earth	Inorganic Natural	Hematite, Fe_2O_3 + impurities (e.g., quartz, clays, anatase/rutile)	Ancient Age – Present	- *Saint Jeremiah* Monastery (4th c.)(*) (Saqqara, Egypt) [181] - Roman wall paintings from *Castulo* (Jaen, Spain) [182] - Frescoes in the tablinum of the House of the Bicentenary at the archaeological site of Herculaneum (Pompei, Naples, Italy) [183]
	Lead red; Minium[a]	Inorganic Synthetic	Minium, Pb_3O_4	Ancient Rome (500 BCE) – Modern Age	- St. Alexander catacombs (2nd - 5th c.) (Rome, Italy) [184] - Twelve Byzantine churches (10th–15th c.) (Mani Peninsula, Greece) [185] - Roman wall paintings from *Castulo* (Jaen, Spain) [186]
	Cinnabar[b]	Inorganic Natural	Cinnabar, HgS, + impurities (e.g., quartz, dolomite, pyrite)	Ancient Greece (1600 BCE) – 20th century	- Etruscan *Tarquinia* wall painted tombs (Tuscia, Italy) [61] - Wall paintings at the *Domus of Octavius Quartio* (Pompei, Naples, Italy) [187] - *San Isidoro del Campo* Monastery (15th c.) (Seville, Spain) [188]
	Vermillion[b]	Inorganic Synthetic	Cinnabar, HgS	Medieval Age – 20th century	- Wall paintings in *Saint Orso Priory* palace (15th c.) (Aosta, Italy) [105] - Wall paintings in Aosta Valley (mid-15th c.) (Aosta, Italy) [107] - Wall paintings in *Santa María de Lemoiz* (Basque Country, Spain) [189]
	Litharge[c]	Inorganic Synthetic	Litharge, PbO	Ancient Age – 1800	- Roman wall paintings from *Monte d'Oro* (Rome, Italy) [190] - Medieval wall paintings from the Monastery of Saint Baudelio (Soria, Spain) [191] - Wall paintings in *Saint Orso Priory* palace (15th c.) (Aosta, Italy) [105]
Green	Green earth[d]	Inorganic Natural	Fe-containing clay minerals: celadonite or glauconite + minerals of the smectite and chlorite group	Ancient Age – Present	- Fresco wall painting of Mariano de Cossío (Canary Islands, Spain) [192] - Church of the *Annunciation of Mary* (13th – 15th c.) (Crngrob, Slovenia) [193] - Frescoes in the tablinum of the House of the Bicentenary at the archaeological site of Herculaneum (Pompei, Naples, Italy) [183]
	Malachite[e]	Inorganic Natural	Malachite, $Cu(CO_3)(OH)_2$	Natural: Ancient Age (2600 BCE) – 19th century Synthetic: 17th century – Present	- *Saint Jeremiah* Monastery (4th c.) in Saqqara, Egypt [112] - Wall paintings at the *Domus Valeriorum* (Rome, Italy) [194] - *Roman site of Cambre* (La Coruña, Spain) [111]
	Chrysocolla[e]	Inorganic Natural	Chrysocolla, $(Cu,Al)_4H_4(OH)_8Si_4O_{10}{\cdot}nH_2O$	Ancient Age – Present	- 2nd m.(*) BC frescoes from the Mycenaen Palace of Pylos [195] - 12th c. frescoes from *Novalesa* Abbey (Turin, Italy) [121] - 13th c. frescoes beneath Siena cathedral (Italy) [173]
	Verdigris	Inorganic Synthetic	Hoganite, $Cu(CH_3{-}COO)_2{\cdot}2Cu(OH)_2$	Ancient Greece and Rome – 19th century	- *Madonna and Child enthroned with Saints* wall painting in St. Augustine church (Siena, Italy) (14th c.) [196] - Medieval frescoes from Saint Baudelio Monastery (Soria, Spain) [191]
	Viridian[f]	Inorganic Synthetic	$Cr_2O_3{\cdot}2H_2O$	Beginning of 19th century - Present	- The *Crucifix Chapel* of *Aci Sant'Antonio* (Sicily, Italy) [148] - Different paintings by Henrique Pousao (1859–1884) (Portugal) [197]
	Guignet green[f]	Inorganic Synthetic	Cr_3BO_6	1838/1859 – Present	- 20th c. Gino Severini (1833–1966) wall paintings (Semsales, Switzerland) [166]
	Chromium green	Inorganic Synthetic	Skolaite, Cr_2O_3	1860 – Present	- Vincenzo Pasqualonis (1820–1880) wall paintings in *Saint Nicola* (Carcere, Rome, Italy) [161] - Juan Miguel Sánchezs wall Paintings in the *Carmen Chapel* (Seville, Spain) [198]

(*continued on next page*)

Table 2 (*continued*)

Colour	Pigment	Nature	Pigment composition	Approx. period of use	Evidence
Blue	Egyptian blue[g]	Inorganic Synthetic	Cuprorivaite, $CaCuSi_4O_{10}$	Ancient Age – Medieval Age (13th century)	- *Knossos* Palace (Crete, Greece) [199] - Wall paintings at the *Domus of Octavius Quartio* (Pompei, Naples, Italy) [187] - Wall paintings at the *Domus Valeriorum* (Rome, Italy) [194]
	Natural ultramarine[h]	Inorganic Natural	Lazurite, $3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2Na_2S$, + impurities	Ancient Age – end of the 18th century	- *Santa Maria di Cerrate* abbey (12th-13th c.) (Lecce, Italy) [200] - Byzantine frescoes at Chora Church (Istanbul, Turkey) [201] - *Servilia* Roman tomb (Carmona, Seville, Spain) [202]
	Azurite[e]	Inorganic Natural	Azurite, $Cu(CO_3)_2(OH)_2$	Natural: Ancient Age (2600 BCE) – 18th century Synthetic: 17th century – Present	- *Assumption of the Virgin Mary* (1526–1530) dome (Cathedral of Parma, Italy) [158] - Byzantine wall paintings in the *Protaton Church* (Mount Athos, Greece) [203] - *Regina Martirium* dome in the *Pilar* Basilica (Zaragoza, Spain) [204]
	Smalt blue	Inorganic Synthetic	Blue potassium glass composed of SiO_2 (65–72 %), K_2O (10–21 %), CoO (2–18 %) + impurities [160]	15th century – 18th century	- *Assumption of the Virgin Mary* (1526–1530) dome (Cathedral of Parma, Italy) [158] -Wall paintings at *Saint Girolamo Chapel* (1560–1564) in the *SS. Annunziata Church* (Florence, Italy) [205] - Antonio Palominos (1655–1726) wall paintings in the *Real Parroquia de los Santos Juanes* (around 1697) (Valencia, Spain) [151]
	Synthetic ultramarine[h]	Inorganic Synthetic	Lazurite, $3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2Na_2S$	1828 – Present	- Vincenzo Pasqualonis (1820–1880) wall paintings in *Saint Nicola* (Carcere, Rome, Italy) [161] - Wall paintings on the *Almada Negreiros* building (Lisbon, Portugal) [178] - Fresco wall painting of Mariano de Cossío (Canary Islands, Spain) [192]
Yellow	Yellow ochre; Yellow earth	Inorganic Natural or synthetic	Limonite, $FeO(OH){\cdot}nH_2O$ (mixture of iron-containing oxo-hydroxides as e.g., goethite- FeO(OH), ferrihydrite $Fe^{c+}{}_{10}O_{14}(OH)_2$, jarosite- $KFe_3(OH)_6(SO_4)_2$) or goethite (with quartz and clay minerals)	Natural: Ancient Age – Present Synthetic: 17th-18th century – Present	- *Knossos* Palace (Crete, Greece) [199] - Roman wall paintings from *Castulo* (Jaen, Spain) [182] - Frescoes in the tablinum of the House of the Bicentenary at the archaeological site of Herculaneum (Pompei, Naples, Italy) [183]
	Naples yellow[i]	Inorganic Synthetic	Bindheimite, $Pb_2Sb_2O_7$	Ancient Age – 19th century Industrially manufacture since 1850	- Wall paintings from a building complex (Caelian Hill, Rome, Italy) [89] - Frescoes painted by Antonio Palomino (1655–1726) (Valencia, Spain) [139] - Wall paintings in the *Baños de Doña María de Padilla* (1565–1579) (Royal Alcázar of Seville, Spain) [188]
	Orpiment	Inorganic Natural or synthetic	Orpiment, As_2S_3	Ancient Age – 8th century Synthetic: 17th century	- *Paestum* archaeological site wall paintings (Capaccio, Salerno, Italy) [206] - Vincenzo Pasqualonis (1820–1880) wall paintings in *Basilica of S. Nicola* (Cercere, Rome, Italy) [161] - Medieval Islamic wall paintings of *Al-Bīmāristān Al-Mu'ayyidi* (Cairo, Egypt) [135]
	Massicot[d]	Inorganic Synthetic	Litharge, PbO	Ancient Age – 19th century	- Wall paintings (12th c.) from the Monastery of *Santa Maria delle Cerrate* (Puglia, Italy) [207] - Medieval wall paintings (10th-14th c.) of the *Santi Stefani crypt* at Vaste (Lecce, Italy) [208] - Wall paintings in *Saint Orso Priory* palace (15th c.) (Aosta, Italy) [105]
	Chrome yellow	Inorganic Natural or synthetic	Crocoite, $PbCrO_4$	Middle Ages – Present Synthetic: 1778	- Vincenzo Pasqualonis (1820–1880) wall paintings in *Saint Nicola* (Carcere, Rome, Italy) [161] - 13th c. frescoes beneath Siena cathedral (Italy) [173] - 20th c. *Pentecostes* by Julio Resende (1917–2011) at the *Church of Nossa Senhora da Boa Esperança* (Canaviais, Portugal) [209]

(*continued on next page*)

Table 2 (*continued*)

Colour	Pigment	Nature	Pigment composition	Approx. period of use	Evidence
Brown	Raw sienna	Inorganic Natural	Goethite, FeO(OH) + quartz + clays	Ancient Age – Present	- *Saint Nicholas Anapafsas church* (Meteora, Greece) [210] - Roman wall paintings in *Villa della Piscina* (Rome, Italy) [211]
	Burnt sienna[j]	Inorganic Natural	Hematite, Fe_2O_3 + quartz + clays	Ancient Age – Present	- *Saint Nicholas Anapafsas church* (Meteora, Greece) [210] - Roman wall paintings from archaeological sites (Judea, Israel) [212]
	Raw umber	Inorganic Natural	Iron and manganese oxides + quartz + calcite + clays	Ancient Age – Present	- *Saint Nicholas Anapafsas church* (Meteora, Greece) [210] - Wall paintings (18th c.) from the Convent of Saint António dos Capuchos (Estremoz, Portugal) [213]
	Burnt umber[j]	Inorganic Natural	Iron and manganese oxides + quartz + calcite + clays	Ancient Age – Present	- *Saint Nicholas Anapafsas church* (Meteora, Greece) [210] - Wall paintings (18th c.) from the Convent of *Saint António dos Cauchos* (Estremoz, Portugal) [213]
Purple	*Caput Mortuum*[k]	Inorganic Synthetic	Hematite, Fe_2O_3 + kaolinite, $Al_2Si_2O_5(OH)_4$	Ancient Rome – Present Synthetic (Mars Violet): since 18th century	- Byzantine wall paintings in the *Protaton Church* (Mount Athos, Greece) [203,210] - *Servilia* Roman tomb (Carmona, Seville, Spain) [202]
White	Lime white[l]	Inorganic Natural	Calcite/aragonite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), chalk (white clay), diatomite ($SiO_2 \cdot nH_2O$)	Ancient Age – Present	- Roman wall paintings in *Thamusida* (Rabat, Morocco) [214] - Medieval frescoes from the Žiča monastery (Serbia) [102] - St. Alexander catacombs (2nd - 5th c.) (Rome, Italy) [184]
	Lead white	Inorganic Synthetic	Hydrocerussite, $2PbCO_3 \cdot Pb(OH)_2$	Ancient Age – mid-19th century	- Wall paintings (12th c.) from the Monastery of *Santa Maria delle Cerrate* (Puglia, Italy) [207] - Wall paintings in *Saint Orso Priory* palace (15th c.) (Aosta, Italy) [105] - 13th century frescoes beneath Siena cathedral (Italy) [173]
	Barium white	Inorganic Synthetic	Baryte, $BaSO_4$	Around 1782 – Present	- 20th c. *Pentecostes* by Julio Resende (1917–2011) at the Church of *Nossa Senhora da Boa Esperança* (Canaviais, Portugal) [209] - *Crowning of the Virgin Mary* from artist Vittorio Fagnano (18th c.) at *Beata Vergine del Pilone* (Piemonte, Italy) [215]
	Zinc white	Inorganic Synthetic	Zincite, ZnO	1834 – Present	- 20th c. Gino Severini (1833–1966) wall paintings (Semsales, Switzerland) [166] - *Rejoicing querubs* from artist Vittorio Fagnano at *Beata Vergine del Pilone* (Piemonte, Italy) [215] - Vincenzo Pasqualonis (1820–1880) wall paintings in *Saint Nicola* (Carcere, Rome, Italy) [161]
	Titanium white	Inorganic Synthetic	Anatase, TiO_2	1916 – Present	- 20th c. *Pentecostes* by Julio Resende (1917–2011) at the Church of *Nossa Senhora da Boa Esperança* (Canaviais, Portugal) [209]
Black	Carbon black[m]	Inorganic Synthetic	Carbon (C)	Ancient Age – Present	- *Knossos* Palace (Crete, Greece) [199] - Wall paintings at the *Domus of Octavius Quartio* (Pompei, Naples, Italy) [187] - Roman wall paintings from *Castulo* (Jaen, Spain) [186]
	Lampblack[m]	Inorganic Synthetic	Carbon (C)	Ancient Age – Present	- Church of the *Holy Mother of God Hodegetria* in Pec Monastery (14th c.) (Peja, Serbia) [216] - *Paestum* archaeological site wall paintings (Capaccio, Salerno, Italy) [206] - Medieval wall paintings from the *Peregrina* Convent (Leon, Spain) [217]

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Table 2 (*continued*)

Colour	Pigment	Nature	Pigment composition	Approx. period of use	Evidence
	Ivory black	Inorganic Synthetic	Carbon (C)	Ancient Age – Present	- *Paestum* archaeological site wall paintings (Capaccio, Salerno, Italy) [206] - Wall paintings from the Roman archaeological site of Cuma (Campania, Italy) [218] - Roman wall paintings from *Castulo* (Jaen, Spain) [182]

*c.: century; m.: millenia.

[a] *Minium secundarium* in Latin.

[b] *Minium* in Latin. Cinnabar is the natural pigment whilst vermilion is the synthetically obtained. It should be noted that the term vermilion has been used in some studies without prior analysis to differentiate whether it is the natural or artificial variant (e.g., the presence of impurities). Therefore, the examples given should be treated with caution.

[c] Litharge (reddish orange) and massicot (yellow), both lead oxide, are often confused or used synonymously in literature. Both are obtained from lead white (litharge around 330 °C and massicot 600 °C) although they are also found as minerals.

[d] Also known as Verona green. *Creta viridis* in Latin.

[e] Green malachite was known as *Chrysocolla* in Greek and Latin. However, chrysocolla is an independent pigment of copper silicate hydroxide hydrate. Synthetic malachite is known as green verditer, as well as synthetic azurite in known as blue verditer.

[f] Guignet green is sometimes improperly confused with Viridian or Emerald green.

[g] During ancient times it had different nomenclatures: c*aeruleum aegyptium; vestorianum; puteolanum* in Latin.

[h] *Caeruleum scythicum* in Latin. Known as ultramarine during the Middle Ages, it was obtained from the mineral lapis lazuli. In the present we differentiate between natural and artificial ultramarine.

[i] It must be pointed out that even though Naples yellow was synthetically obtained in 1850, it was already artificially prepared in Antiquity.

[j] The so-called "burnt" pigments are obtained from calcination of their raw counterparts, i.e., burnt sienna from raw sienna and burnt umber from raw umber.

[k] *Usta purpurissimum* in Latin.

[l] *Bianco sangiovanni* in Italian, a calcium carbonate that can appear in the form of calcite, vaterite or aragonite. Nowadays, calcite is mainly used as an inert pigment, mixed with other mineral pigments [15,203].

[m] Both carbon black and lampblack are obtained from burning fuels (gas, fats, asphalt, etc.). However, lampblack is obtained specifically by burning oil in a lamp.

used during the Bronze Age, red and yellow ochres (i.e., hematite-Fe_2O_3-, goethite- FeO(OH)- or limonite- $FeO{\cdot}nH_2O$-), carbon black and Egyptian blue ($CaCuSi_4O_{10}$) were used [28,34,36], probably obtained from local sources [37]. Other compounds have been found to be used as blue pigments during this period such as iron-rich minerals (e.g., riebeckite-$Na_2Fe^{2+}{}_3Fe^{3+}{}_2(Si_8O_{22})(OH)_2$-) [37].

Classical Antiquity

The painting technique later spread throughout Ancient Greece (1200 – 323 BCE), as can be seen for example in *Women at work* at the Akrotiri archaeological site (Santorini, Greece) [38]. During the Hellenistic period (4th – 3rd c. BC) there was a phenomenon of decorating tombs with fresco wall paintings such as the *Tomba di Cavalieri* (Ancient Apulia, southern Italy) [39] or several tombs from Ancient Thrace (southern Bulgaria). In the latter, up to three layers of plaster were encountered [40]. In short, archaeological evidence from this period shows the high quality of the rendering on the mortar surface during this period, as can be seen in the hunting scene frieze in the Tomb of Philip (Vergina, Greece), and in other frescoes from the Macedonian period [41]. In terms of fresco pigments, the main contributions made by the Greeks were lead white ($2PbCO_3{\cdot}Pb(OH)_2$) and lead red (Pb_3O_4), the latter known as *minium* after the River Minho in northern Spain [42]. Both were found in a Greek villa in the archaeological site of Tel Anafa (Galilee, Israel) together with exported pigments like Egyptian blue or yellow ochres, i.e., earth pigments from hydrated forms of iron oxide, which the Greeks called *ochra* [43]. Even though these pigments may have been exported to Greece, there is evidence that Egyptian blue was one of the main products manufactured during the Hellenistic period in the ancient town of Kos (Island of Kos, Greece) [44] together with other earth pigments such as hematite-based red earth (Fe_2O_3), yellow ochres (goethite-FeO(OH)-, ferrihydrite-$Fe^{3+}{}_{10}O_{14}(OH)_2$- and jarosite-$KFe_3(SO_4)_2(OH)_6$-) and green earth (Fe-containing clay minerals: celadonite-$K(Mg,Fe^{2+})Fe^{3+}(Si_4O_{10})(OH)_2$)- or glauconite-$(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$-, and minerals from the smectite and chlorite group) [44]. It must also be considered the use of local minerals as pigments during this period. Even though the wall paintings at the monumental cist tomb in Pella (Macedonia, Greece) are thought to be executed following a secco technique, the minerals vanadinite ($Pb_5(VO_4)_3Cl$) or conichalcite ($CaCu(AsO_4)(OH)$) were encountered mixed with lead white [45]. These two minerals were also found in tombs from Hellenistic Alexandria (Egypt) [46]. In addition, pigment manufacture is well documented during the Hellenistic period in Ancient Greece where *Liber De Lapidibus*, a treatise by Theophrastus (372 – 286 BCE), is of particular interest in that it summarizes the state of knowledge on stones, minerals, gems, and earths [47,48]. It describes the production of two ancient pigments, Egyptian blue (*egyptios kyanos*) and lead white (*psimythion*) [49].

Throughout the 9th and 8th centuries BC, people from the Mediterranean Levant settled in different territories bathed by the Mediterranean (Cyprus, the Maghreb, Sicily, Sardinia, Ibiza and the Iberian Peninsula) giving rise to the Phoenician culture [50], known as Punic from the 5th century onwards. Carthage (actual Tunisia) became the major political power in the Mediterranean until Roman conquest (2nd century BC) [50]. Despite their influence in the Mediterranean, wall painting was rare in Phoenician contexts, surviving principally in tombs [51]. On the one hand, one of the few examples that can be related to this culture is the so-called Sidonian tomb at Maresha (Shfela, Israel), where the ornamental decoration can be related to Hellenistic and Phoenician styles [52]. On the other hand, the use of cinnabar was found in several burial chambers in the region of Kroumirie (Western Tunisia) [53], known to be used together with hematite as a cosmetic powder during this period [54]. The Sidonian tomb decorative style and the use of cinnabar in Kroumirie are good evidence of the intercultural exchanges that were happening at the time. Probably, the most interesting contribution to posterior painting is the so-called Punic wax, invented by Carthaginians for their ships [55]. Its elaboration and use were described by Pliny and Vitruvius as a binder (painting technique known as *ganosis*). Although it has been found as binder in Roman art [55], beeswax has only been detected in ceramic vessel in Punic Sardinia [56], but not in wall paintings.

The fresco technique was later employed by the Etruscans (around 800 – 300 BCE) also to decorate their tombs [57], as in *The Tomb of the Swimmer* in the Paestum archaeological site (Salerno, Italy) [58]. Due to the posterior Roman occupation, not many wall paintings remain from the Etruscan period. The few remnants that have survived are those preserved in burial sites, i.e., necropolis [59–61]. Tarquinia (Viterbo, Italy) is one of the most important due to its extension (up to 200 tombs), highlighting *The tomb of Orcus* where a mixture of cinnabar and red ochre (hematite) was encountered, as well as the presence of Egyptian blue or yellow ochre [60]. Regarding the preparation of the wall, Steingräber clearly distinguished between three periods [62]: i) the Orientalizing period (7th and 6th c. BC), of Asian and Corinthian influence, with the use of three basic colours (red, yellow and black) applied directly onto a stone wall; ii) the Archaic period (6th and 5th c. BC), with a pictorial palette enriched with green and blue pigments applied in a rudimentary form of *a fresco* onto a thin layer (1 – 3 mm) made of clay, a non-specified stone powder and vegetable fibres, followed by a thin layer of lime paste; and iii) the Hellenistic period (4th and 3rd c. BC) with a thicker layer (up to 3 cm) composed of three layers i.e. the bottom of pozzolana, the second of limestone and siliceous sand, and the last of calcium carbonate.

The technique was substantially improved during the Roman period (around 750 BCE – 476 AC) and spread throughout the Empire. Sometimes the frescoes were retouched *a secco*, using four clearly differentiated artistic styles known as the first, second, third and fourth Pompeian styles (the first inherited from Hellenistic Greeks [63]). The tradition of combining fresco and secco was rather recurrent, as seen in the Roman city of *Emona* (actual Ljubljana, Slovenia) [64]. The most representative examples of fresco wall paintings due to their exceptional state of preservation are in the Pompeii [65,66], Herculaneum [67] and Stabiae [68] archaeological sites (Naples, Italy), which are outstanding not only in terms of quantity, but also of quality [6]. Pliny the Elders (23 – 79 CE) *Natural History* [69,70] is considered an essential source for those wishing to understand the role played by wall paintings in Roman society, described as expressions of the luxury and wealth of the *dominus* as seen in the Mt. Vesuvius area. He also mentions numerous distinguished Greek painters (i.e., Panaenus, Apollodorus or Apelles among others) [8,71], although for our purposes the most valuable information appears in the last two chapters which deal with mineralogy and art [70]. Another important contribute into the knowledge of Roman mortars and stuccoes is Greco's work [72], where he compiles Latin bibliographical sources (from the 2nd c. BC until 5th c. AD) regarding this topic.

Perhaps the most important bibliographical source on architecture in ancient times is Vitruvius (80–70 – 15 BCE) and his *De architectura* [73,74]. Composed of ten books, the seventh (Vitr. *arch.* VII) contains information on the stucco technique and the preparation of the walls [8,74]. Vitruvius also specified that lime has three functions: a) as a bond between stones and bricks; b) for plastering (stucco) as a means of protecting and/or decorating surfaces; and c) as a base for mural painting, flooring, and mosaics [12]. According to Vitruvius, wall paintings should be composed of seven layers. However, only in Rome there are few surviving examples that seem to have followed this rule [75]. And whilst in various provinces of the Roman Empire (e.g., *Ostia Antica* in Italy, *Carnuntum* in Austria and *Ephesus* in Turkey) the Vitruvian rule of applying more than one layer of *intonaco* (explained further bellow) was followed [76], this did not always occur in other provinces. For instance, a series of Roman wall paintings from Aquileia (Italy) which span a period of over six centuries have shown that they completely differ between one another regarding the number of mortar layers and their thickness [77]. Yet, the materials used were always the same and from local provenance [77].

As regards the constituent materials, during the Roman Empire it was easy to locate and extract suitable calcitic stone materials (*lapidem bonum* or 'good stone'). The method for obtaining the lime consisted of calcinating calcitic stone such as white stone (*albo saxo*), travertine (*tibertino*), etc., at a temperature of around 900 °C in order to obtain quicklime or calcium oxide (CaO). The person responsible for firing the stone was known as the *calcarius* [73,74,78]. This process is well described by the Roman author Marcus Porcius Cato (Cato the Elder: *On agriculture,* XXXVIII [5]). To obtain a lime mortar, quicklime (*calx viva*) must be mixed with water in a slaking process to produce slaked lime (referred to as *calx macerata* by Vitruvius [74]) or calcium hydroxide ($Ca(OH)_2$) via an exothermic reaction. Different ancient sources generally recommend slaking the lime for between two and three years [6] to obtain a high-quality slaked lime. This process must be carried out to remove any lumps of calcium oxide that could damage the mortar due to later hydration [5,73].

The aggregates used during this period varied according to their geological area, as most came from local sources [79]. In Roman construction, *caementa* was understood as coarse aggregates [18]. It was also known that, if not properly and repeatedly washed, using sea sand (*harena marina*) as an aggregate caused the formation of saline efflorescence, which is why river sand (*harena fluvialis*), e.g., quartz-based sands, was preferred. However, other aggregates such as pozzolanic sands (*harena fossicia*) and crushed terracotta (*testae tunsae*), characteristic of the Roman period, can also be found in mortars [79]. According to Vitruvius, marble powder (*opus marmoratum*) could also be used in the final layers of stucco to provide a whiter, smoother, more lustrous appearance [73]. It should be noted that the use of marble powder can be traced back to the Mesopotamian period, as in the palace of Yarim-Lim in the archaeological site of Alalakh (Antakya, Turkey) [6,80]. However, no petrographic characterisation was carried out in these studies to precisely identify the type of aggregate based on the morphology, structure, and size of the crystals, and therefore the exact lithotype cannot be asserted.

The execution procedure of a wall painting was perfected during the Roman era where stuccoes were referred as *opus tectorium, opus albarium* or *gypsum* depending on material composition, workmanship and utility (i.e., inside or outside of the architectural building) [81]. In relation to wall paintings, the master builder (*redemptor*) was accompanied by specialized craftsmen (*tectors*), who applied successive layers of mortar (*opus tectorium*) to smoothen the rough surface of the wall (i.e., stucco). The mixture of binder and aggregates was known as *calx harenata* ('sanded lime'). According to Vitruvius, the procedure was as follows: first the *arriccio* (*harenatus*), composed of several layers of mortar, was applied to smooth the rough surface of the base wall. This was followed by several more layers of *intonaco* to homogenise the surface and, lastly, the *intonachino* or painting layer. The layers were applied with an increasingly fine-grained aggregate from the innermost to the outermost layer [6,16,81]. Some authors, such as Vitruvius and Faventinus, also refer to an additional final stage in which the final layer was polished (*politiones*) to make it more resistant [73]. The outlines of the decorations were drawn by wall painters (*pictores parietarii*) and then a figure painter (*pictor imaginarius*) carried out the more complex artwork [8,73].

The *fresco* painting itself was created with pigments (from the Latin *pigmentum*) that had previously been mixed with water. These were applied with a brush onto the fresh fine-grained lime-based plaster (calcium hydroxide, $Ca(OH)_2$) or *intonaco*. The pigment particles became bonded to the surface when the calcium hydroxide reacted with atmospheric carbon dioxide (CO_2), so creating a compact, resistant film of calcium carbonate ($CaCO_3$) that protected the pigment [7,8,82], so making the paints more durable [8,14] or 'permanent' according to Vitruvius [6]. Ever since ancient times, inorganic pigments (minerals) have been preferred to organic pigments in fresco painting because they can withstand the alkaline environment of lime mortars [7]. Inorganic pigments are either native earths or calcined native earths, obtained from mechanical processing and separation. There were also inorganic synthetic colours obtained artificially from chemical reactions between different raw materials [16,83]. Most of the traditional pigments used since ancient times are still a common feature of the painters palette today, although some have fallen into disuse [84].

Romans used the same pigments as the Egyptians and Greeks i.e., Egyptian blue, named by the Romans as Alexandrian blue, among other terminologies, or green-earth pigments, the latter were obtained by the Etruscans from glauconite, celadonite and chlorite [85,86]. It is thought that the earliest Roman frescoes were painted with pure pigments such as yellow and red ochres, carbon blacks, and whites such as calcite/aragonite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), chalk (white clay), diatomite ($SiO_2 \cdot nH_2O$) and lead white as mentioned by Pliny and Vitruvius [85,87]. One of the most important pigments was cinnabar (HgS) (*cinnabaris* in Latin), which according to authors like Vitruvius was obtained from mines in Almaden (Ciudad Real, Spain) [42,85,88], and has been found in numerous wealthy Roman houses such as in a *domus* on the Caelian Hill (Rome, Italy) [89], all around Mount Vesuvius [90] and in other places in the Roman Empire such as King Herods Palace in Jericho (Jerusalem, Israel) [91]. Also, in a fresco fragment preserved at the National Archaeological Museum of Naples (Italy), small particles of lazurite (from the mineral lapis lazuli) were promptly identified [90], as in the pigment named by Pliny [69] *Caeruleum Scythicum*. The name derives from the Scythian traders (region located in the northern coasts of the Black Sea) who exported to the Mediterranean [48,92], another clear reference of the commercial trade that happened at the time.

As for the production of synthetic pigments, the conversion of magnetite to hematite by calcination was described by Dioscorides (40 – 90 BCE) in *De materia medica* [93]. It therefore seems likely that the Romans obtained various ochres from iron metal [94], as also happened in Ancient Greece [44]. Many examples of the use of such ochres are drawn out on Table 2. Vitruvius [74] also explained the reaction whereby acetic acid (vinegar) was poured onto copper sheets so as to obtain copper green, also known as *verdigris* ($Cu(CH_3{-}COO)_2 \cdot 2Cu(OH)_2$) (*aeruca* in Latin), considered as a partially organic pigment and therefore theoretically not suitable in alkaline environments [95]. However, it has been found to be part of the pictorial palette of an extensive collection of fresco fragments from several roman villas in Burgos (N Spain) [96]. The purple pigment known as *caput mortuum* was also identified as part of the palette [96], a pigment obtained from iron oxides and hydroxides with a high presence of clays (above 80 %) [97]. However, although this pigment was not mentioned by Pliny nor Vitruvius, Pliny does mention the production of a purple pigment called *usta, ostrum* or *usta purpurissimum* [69] obtained by heating hematite with acetic acid, covering a wide range of colours (from red to deep violet) [98]. This pigment was indeed encountered, although on Romano-British wall paintings, presenting a similar composition to *caput mortuum* [98]. Finally, Vitruvius [74] also described the production of lead white following a similar procedure to *verdigris* but with lead sheets [74], found in wall paintings from the Vesuvian area [90].

Mediaeval age

The literature of the Middle Ages often consisted of a compendium of texts reviewing previous ancient works, including technical treatises, recipe books and iconographic catalogues. New considerations were also included, together with theological reflections in that art was regarded as a way of praising God, and colours were used with symbolic meanings [7]. Compared to the Roman tradition of seven layers of mortar, in the early Middle Ages (5th-10th centuries), fewer preparatory layers (normally just two) were applied [7]. Straw could also be used as an admixture, added to the *arriccio* to facilitate carbonation [99]. This is recurrent during the Byzantine period (312–1453) [100,101] and in the Mediterranean [7], observed in medieval frescoes such as those in the Žiča monastery (Serbia) [102]. During the long period of the Byzantine Empire the wall painting technique did not change much, except for a more accurate preparation of the wall [7].

One of the oldest and most relevant early mediaeval treatises were *Mappae Clavícula* (8th century, with its 12th century version known as *Phillipps manuscript*), which contains recipes for materials of art and craftsmanship [101,103], and *Compositiones variae* (late 8th century), also known as the *Lucca manuscript* [7]. The first describes in detail the preparation of different pigments (e.g., azurite, vermilion, white or red lead) and specifies the use of a lime obtained from the calcination of limestone, travertine or marble [103]. The second focuses on the fresco technique as no organic binder is mentioned in the application of the pigments, consisting of a collection of recipes with instructions on how to prepare and use pigments such as vermillion (HgS), i.e., artificial cinnabar, which was prepared by heating mercury and sulphur, although many of its recipes derive from the classical period [7,101,104]. This pigment was found in *Saint Orso Priory* palace in Aosta, Italy [105]. However, the authors make the assignment of the artificial variant on the basis of the absence of impurities (common in natural cinnabar). Therefore, other features should be analysed, such as pigment morphological appearance and particle grain size, being however difficult to differentiate between natural cinnabar and synthetic vermilion when the latter has been obtained by dry method (i.e., by sublimation) [106]. Additionally, the most used copper carbonate pigments used during the Medieval period, that is blue azurite ($Cu(CO_3)_2(OH)_2$) and green malachite ($Cu_2(CO_3)(OH)_2$), were found in the in the Saint-Maxime oratory (Aosta, Italy) [107]. Their synthetic analogues (manufactured in the 17th century) were known as mountain blue and mountain green respectively [108–110]. In fact, copper carbonate pigments have been used since Antiquity, for example in the Roman archaeological site of Cambre (La Coruña, Spain) [111] and in 4th century Coptic frescoes from Saint Jeremiah Monastery (Saqqara, Egypt) [112].

During the High Middle Ages (11th-13th centuries) and the Romanesque period *a fresco, a secco* and *mezzo fresco* techniques were used, although *a fresco* was by far the most widespread. During this period, wall paintings from different parts of the Mediterranean shared many features, leading some researchers to view *fresco* as the first international style [7,24]. Important art treatises included for example *De coloribus et artibus Romanorum* by Heraclius (around 11th century), who showed a keen interest in practical aspects of classical Roman art and offered detailed descriptions of pigment recipes [7]. *De Diversis Artibus* by Theophilus (early 12th century) also deserves a mention as the first treatise written by an artist. It was an important work of reference throughout the Middle Ages and included descriptions of the different methods and painting techniques used by mediaeval artists [113,114]. As well as offering instructions on to how to prepare colours, he also provided theological justifications for the use of certain pigments (for example the use of ultramarine to paint the clothes worn by the Virgin Mary) and described the creative process behind Romanesque art [115]. The Pyrenees has a remarkable collection of Romanesque buildings of very high quality, such as the Church of Santa Eulalia de Unha (Lerida, Spain), where vermilion was presumably found together with other red pigments (hematite and lead red) in fresco wall paintings [116]. The murals in the Abbey Church of Saint-Savin-sur-Gatempe (Saint-Savin, France) [117,118] are also of note. They were also painted on two layers of plaster with coarse sand of different colours due to the presence of iron compounds. Lastly, is interesting to point out the discovery of a rare silicate, from the pyroxene group, known as aerinite (from the Greek *aerinos* meaning blue-sky). This mineral was used as a blue pigment in Romanesque frescoes in Andorra and Catalonia (NE Spain) [119], as well as in Aragon (N Spain) [120], thought to be from local provenance (Pyrenees region). Another example from the area is the 12th century frescoes from *Novalesa* Abbey in Turin, Italy [121].

During this period, Islam was expanding across the Mediterranean (7th-15th centuries). Starting in the Arabian Peninsula, the Muslim conquest extended across the Mediterranean, occupying large parts of the Iberian Peninsula, North Africa, and the Near East. Apparently, they also used frescoes as decoration and the preparation of walls with lime mortars was described by authors like Ibn Jhaldun (1332 – 1406) [122,123]. As happened during ancient Rome, in the countries under Muslim rule, the lime mortars used in frescoes varied over the centuries in terms of both quality and thickness, often including straw [123]. Just like the Romans before them, Islamic artists employed natural earths and minerals as pigments. Their palette had two main colours, hematite for red, and calcite for white, as found in the *Real Alcázar* in Seville (Spain) [124,125]. Although they were painted using the *fresco* technique, the *secco* and *mezzo fresco* techniques were also common during this period, as can be seen in the Alhambra complex (Granada, Spain), widely considered as the best preserved Islamic civil construction from the Middle Ages, where hematite was again used as red [126].

If we return to the advances in fresco techniques, in the late Middle Ages (14th-15th centuries), there were innovations in terms of style, technique, and purpose [7]. It was during the Italian *Trecento* (14th century) that the fresco technique began to spread throughout Europe [6]. Much of the painting was inspired by Byzantine fresco art [24]. As regards the methods for preparing the wall, the Roman techniques were developed, and significant technical and stylistic innovations were made. As compared with ancient wall paintings, these murals had fewer and thinner base layers: two layers as opposed to the seven recommended by Vitruvius [7], as seen throughout the Middle Ages. Additionally, Mora et al. [20] stated that Italian *Trecento* frescoes were substantially better in terms of surface and texture than their Roman, Byzantine, and Romanesque counterparts. After the break-up of the Roman Empire, even though early medieval craftsmen used the same methods and materials as their predecessors, they were not as careful in the selection of materials. There seems to have been a collective loss of knowledge regarding the procedures for obtaining lime [18,19], with a consequent decline in the quality of the mortars in terms of compactness and homogeneity. However, lime-based mortars were still widely used [127] and the Roman method of painting *a fresco* and then doing the final retouching *a secco* remained popular. Other procedures like polishing the surface (*politiones*), mentioned by Vitruvius, were also used, for example in the Byzantine paintings of *Dormition of the Virgin,* in the Monastery of Santa Maria del Rogato (Sicily, Italy) [128]. Overall, a decline in mortar quality is evident, as is the presence of unburnt relicts in at the 15th century wall paintings from the archaeological site of St. Maria Veterana (Triggiano, Italy) that suggests a non-homogeneous calcination temperature of the lime [129].

During this period, large-scale frescoes were executed, in which the plaster was applied according to two different systems. The first was *pontate*, meaning ‘scaffolding’, in which the mortar was applied in horizontal sections corresponding to the area reachable from the scaffold. This system was the most common until the 13th century [7,101]. The second method was called *giornata,* meaning ‘a working day’, and involved the application of smaller sections of different sizes for more detailed, more refined paintings [7,101]. This system was also applied during the Roman period [8,87], although it did not become common until the Middle Ages, as seen in the frescoes in Saint Britius church in Volarje (Tolmin, Slovenia) [130].

Greek Panselinos is the author of the 13th century wall paintings at the Protaton Church (Mount Athos, Greece), painter known as one of the finest representative scholars from the Macedonian iconographic school. He followed the age-old Byzantine tradition of wall painting [131]. The method used by Panselinos is described in the 18th century by Dionysios of Fourna who explains that he used limewater and/or lime as binder to paint over wet mortar (i.e., fresco) [131]. This is the first time that a binder is mentioned as being used to paint *a fresco.*

It was around this time that the first treatise on art written in a vernacular language appeared. It was written by Cennino Cennini (around 1370 – 1440) [132] and is considered the main source of knowledge on the fresco technique, on which it had great influence during the late Middle Ages and Renaissance. The book describes workshop praxis, wall preparation, and pigment manufacturing procedures [7,132,133]. Cennini believed that Roman fresco was the ideal form and referred to the technique for the first time as *buon fresco* (literally ‘good fresco’), which he claimed was ‘the most agreeable and impressive kind of work’ [132]. At this point, and largely thanks to Cennini, the artistic merits of fresco painters such as Giotto (1267 – 1337) were becoming increasingly widely recognised. Examples include his *Annunciation* painting in the Arena Chapel (Padua, Italy), in which he used ground marble in the paint layer (*intonaco*) [7], as in the Roman period. Cennini heralded Giotto as the initiator of an unprecedented artistic revolution in terms of imagination and creativity, and for developing a painting technique that simulated marble slabs related with Vitruvius *politiones* [7]. By the end of the 14th century the International Gothic Style emerged. The frescoes in this style were characterised by many refined details added by retouching in *secco* [7].

During the Middle Ages, many of the pigments used since ancient times fell into disuse and were replaced by new pigments. The range of colours increased considerably between the 9th and 15th centuries due to chemistry research [85]. The most important blue pigment was made from the mineral lapis lazuli ($3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2Na_2S$) [42,134], known as natural ultramarine, from the Italian word *oltremare* meaning ‘overseas’, since it came from Afghanistan [134]. Together with azurite they replaced Egyptian blue. Other pigments worth mentioning include orpiment yellow (As_2S_3) [85], as found on the Islamic fresco wall paintings at *Al-Bīmāristān Al-Mu'ayyidi* (Cairo, Egypt), mixed with azurite [135], although only Arabic gum and animal glue was ruled out, whereas other organic binders could have been used such as egg yolk. Finally, it is important to highlight that Cennini [132] referred to green earth as *verdeterra*. This is sometimes confused with the *creta viridis* cited by Vitruvius and occasionally translated as *verditer*, which is a basic copper carbonate ($2CuCO_3{\cdot}Cu(OH)$), and therefore an entirely different pigment [86,92]. As for white, Cennini [132] referred to calcium carbonate as *bianco sangiovanni,* an umbrella term within which mineralogists would classify calcite, aragonite and vaterite [136].

Modern age

The Renaissance *Quattrocento* (15th century) and *Cinquecento* (16th century) brought a new boom in fresco wall painting with artists of the stature of Michelangelo (1475 – 1564) and his masterpiece, the Sistine Chapel (Vatican City) [137]. The term ‘Renaissance’ comes from the Italian *rinascita* (rebirth) marking the revival of the arts [138]. It was a period of great advances in terms of technique, with numerous artists developing and experimenting with pigments and mixtures thereof [139]. Perspective and proportion were also improved [24]. The Italian Renaissance quickly spread to other countries leading to further important artistic developments. During this period, the mural bases varied with changes in the thickness and composition of the different mortar layers (*arriccio* and *intonaco*) [7]. These changes can be observed for example in the frescoes by Master Bolfgang in the churches of Crngrob (1453), Mirna (1463–1465) and Mevkuz (1465) in Slovenia. In the first, he used a low-quality mortar with sand, whilst in the other two he used marble powder [140]. This shows that the techniques used by individual artists evolved over the course of their careers with mortars of different composition and characteristics.

In his architecture treatise, *De re aedificatoria* [141], Leon Batista Alberti (1404 – 1472) advises on several aspects of the method for obtaining lime. For instance, he explained that the limestones should be fired for a minimum of 60 h and that the lime should be slaked immediately after obtaining the quicklime to maintain its strength [73]. Like Vitruvius, he also made recommendations about the aggregates, stating that sea (beach) sands should not be used due to the presence of soluble salts and that river sand was the most suitable for rendering [141]. However, most artists used their own materials and developed their own painting techniques. In Italy, the late 15th century was a period of great experimentation with materials, in which egg-yolk binders were gradually replaced by drying oils, which Alberti considered more resistant to decay [142]. Whilst Michelangelo remained loyal to the traditional fresco technique, artists like Leonardo Da Vinci (1452 – 1519) opted for the oil-based technique as can be seen in his *Last Supper* (1495 – 1498) in Santa Maria delle Grazie (Mila, Italy) and his *Battle of Anghiari* (1504 – 1505) in the Palazzo Vecchio (Florence, Italy), fresco wall paintings in which he incorporated *secco* applications with oil [142,143]. However, Da Vinci also painted using the *fresco* technique, as seen in his *Monochromo* (1498) [144].

It was also during this period that Vitruvius *De architectura* was translated and reappraised by authors like Giorgio Vasari (1511 – 1574), and the so-called *buon fresco* became widespread throughout Europe [7,8]. Other ancient treatises were also republished, such as the treatise by Theophrastus which was translated for the first time into modern Italian by Ferrante Imperato (around 1525 – 1615) [47]. In this way, classical techniques were recovered and properly appreciated. Vasari described fresco artists as ‘the finest and most masterly’ as the painting had to be completed in one day [113]. His *Lives of the Most Excellent Painters, Sculptors, and Architects* [145], which contains a series of biographies of 16th century Italian artists, is considered one of the most influential sources on the Italian Renaissance and one of the fundamental texts in art history. Even though he viewed *a fresco* as the most popular technique, he also reported that *secco* paintings became increasingly widespread from the mid-16th century onwards [145]. Additionally, advances in perspective during this century led to the emergence of cartoons, square sheets of paper on which the artist could prepare the drawing, which he then transferred onto the wall. They replaced *sinopia*, i.e., preliminary drawings/sketches executed with iron-based pigments known at the time as *sinopic red ochre*. Cartoons became popular in *Trecento* frescoes because they enabled the artist to create more complex compositions [114,146].

By the Baroque period (17th-18th century), artists had fully mastered the fresco technique, which in addition to walls was used to cover domes and vaults. These more complex surfaces required adaptations in the texture of the mortar and the pigment [6,24]. Other innovations included the application of an opaque mass of varying thickness of paint known as *impasto* (paint is applied thickly and stands out from the surface, as in oil paintings) [20]. This technique was described in detail in different treatises such as *Perspectiva pictorum et Architectorum* [147] by Andrea Pozzo (1642 – 1709). To achieve this effect, pigments had to be previously mixed with a binder such as lime, as it can be seen in the 18th century frescoes at *Aci Sant'Antonio* (Sicily, Italy) [148]. In his explanation about the preparation of the wall he described two mortar layers, the *arricciato* and the *intonaco.* He also recommended using cartoons of the same size as the intended painting, in which any errors appreciable from a distance (for example incorrect proportions) could be detected and corrected [147]. Pozzo also designed and executed the frescoes at the vault of the church of *Sant'Ignazio* in Rome (Italy) considered as one of the finest examples of the so-called Baroque *quadratura* or *di sotto in sù* (Italian expression that can be translated as “from bellow, upwards”). This is related with a decoration technique based on the spatial effects used to create the illusion of a three-dimensional space [149].

Treatise on Painting [150] by the Spanish artist Antonio Palomino (1655 – 1726) offers interesting insights into fresco painting during the Baroque period. It provides advice about the preparation of the wall (e.g., recommending the use of a non-argillaceous sand in the mortar mixture) or the suitability of certain pigments in frescoes. For instance, he suggests not using *Verde Montaña*, i.e., green malachite, a copper carbonate. However, he doesn't refer to the other commonly used basic copper carbonate (i.e., azurite) which he indeed used mixed with green earth in his fresco wall paintings in the church of *Sant Joan del Mercat* in Valencia, Spain [151]. At this point we must stress that Palomino stated in his treatise [150] that azurite could be used in frescoes if combined with green earth to avoid alterations. Additionally, he also suggested to mix milk and azurite to minimise degradation. This recommendation was confirmed through the identification of traces of amino acids that were assigned to the use of casein [151]. In this regard, Palomino would be the first author suggesting the use of an organic binder (milk) to paint with azurite in frescoes.

The information regarding aforementioned Panselinos wall painting technique is found in *The Painters Manual* [152], by the Greek painter Dionysius of Fourna (1670 – 1744), the first manual on Eastern Orthodox painting considered as an indispensable source of Orthodox Christian iconography and Byzantine and post-Byzantine technical practices [153]. Dionysius also dedicates part of his guidebook to the preparation of the wall (i.e. stucco). For this, in order to have a mixture fit for rendering, he recommends the mixture of lime and water with straw and tow, leaving it for two-three days before applying it [101].

As for the fresco painters palette, it was full of well-defined colours, to which, the umbers (raw and burnt umbers, i.e., hydrated iron and manganese oxides) [42] had recently been added according to Vasari [145]. He also stated that “all fresco pigments should be earths, not minerals, and that white should be obtained from calcined travertine” [113]. This can lead to confusion since earth pigments may originate from different minerals (e.g., green earth from celadonite or glauconite minerals). Bone white, obtained by burning bones, was also used as an alternative for lead white. At this time, the term *minium* was used interchangeably to designate lead red and cinnabar pigments, leading to confusion [42]. This pigment has been found in several 16th century frescoes from the so-called *Ribera Sacra* (Galicia, Spain), although completely blackened by the formation of lead dioxide, probably due to its instability in alkaline environments [154]. However, it has been a pigment used since Antiquity (Table 2). Naples yellow ($Pb(SbO_3)_2$) was also developed during this period [42] and, although Cennini already advised about its unsuitability for the fresco painting technique [132], it has been found in the aforementioned *Sant Joan del Mercat* frescoes [155]. Still, it must be pointed out that organic molecules were identified in some of the samples studied. These were related to by-products (i.e., oxalates) derived from cyanobacterial colonisation [155]. Therefore, *a secco* technique should not be dismissed since oxalates can be considered as by-products of the deterioration of organic binders [156].

During the Renaissance, new pigments were created thanks to advances in glass production technology, so creating a more refined colour palette. In the 17th century, further advances in alchemy significantly increased the diversity of the pigments and dyes on the market [85,157]. However, historical pigments were still being used *a fresco* and *a secco*, e.g., lime white, yellow and red natural ochres, and azurite, as can be seen in churches in Crngrob, Mirna and Mevkuz in Slovenia [140]. Simultaneous use of natural ultramarine and azurite was also common [85]. Natural ultramarine was one of the most expensive, most exclusive pigments, and was often used in paintings of the Virgen Mary where it was associated with purity [42], as seen for example in Correggio's *Assumption of the Virgin* (1526 – 1530) in Parma Cathedral (Italy) [158]. At the time, smalt blue (blue potassium glass) also appeared as a possible substitute to expensive natural ultramarine [159]. The term 'Verona green' (*terra verde di Verona*) also began to be used during this period, as early as 1574, to refer to the green earth pigment. It was named after the city of Verona, in northern Italy, the most famous historical source for this compound [86].

Contemporary age to the present

At the beginning of the Contemporary Era (18th century – present), the fresco technique went into decline as wall-covering tapestries came into fashion [6]. Moreover, the use of lime mortars fell into disuse due to the discovery at the beginning of the 19th century of Portland cement, a binder that set much more quickly than lime and had better mechanical properties. By the end of the industrial revolution, traditional lime-making techniques had almost completely disappeared in Western countries [5,12]. In addition, the stucco practice changed: the addition of cement dust and other additives in decorative and finishing works (e.g. plastering walls) enabled reducing the working time and the hardening process of the material [160]. However, there were still a few artists who continued to follow the fresco wall painting models of the *Quattrocento* [1,6], such as Italian painter Vincenzo Pasqualoni (1820 – 1880), who painted *a fresco* in the Church of *Saint Nicola* in Carcere (Rome, Italy) (1865 – 1866) [161]. Furthermore, during the second half of the 19th century and the 20th century, many public buildings (e.g., theatres, museums, opera houses), including the Opera house in Ljubljana (Slovenia), were painted *a fresco*, although many of the artists concerned did not have sufficient knowledge to make durable frescoes [162].

In 1880 a new wall painting technique appeared, which Gambier-Parry dubbed *Spirit Fresco,* in which the colours were applied in the form of varnishes (i.e., non-drip), practically locked up in wax. This form of wall painting was only used in the United Kingdom), as in *The Leighton Frescoes* in the Victoria and Albert Museum (London, United Kingdom) [16,163]. However, its poor resistance and other disadvantages meant it had little impact in other European countries and soon disappeared [16]. Around this time, many books on fresco wall paintings were published. Most of these were bibliographical reviews based on existing documentation and so should be considered more as art textbooks than as treatises. In his *Fresco Painting, Its Art and Technique* [163] James Ward (1851 – 1924) described how to prepare a wall to paint *buon fresco*, recommending an *intonaco* with a 1:3 lime/sand ratio, using very fine, well-washed river sand. This is the first literary source to recommend a painting layer with a high aggregate content (normally it is 1:1 or 1:2, Table 1). He also included a fresco palette with traditional pigments, such as lime white, while also reporting, for the first time, new synthetic pigments such as chromium green (Cr_2O_3) and emerald green ($3Cu(AsO_2)_2{\cdot}Cu(CH_3COO)_2$), the latter also known as Paris green or Veronese green (not to be confused with the Verona green mentioned above) [164].

In *The materials of the artist and their use in painting* [14], Max Doerner (1870 – 1939) made various recommendations concerning the necessary preparations before beginning a fresco, insisting that the artist should consider the ideal time of the year, and the different environmental factors that might come into play. He recommended slaked limes at least twenty years old as the best supports on which to paint, as they had better plastic properties and reactivity towards carbonation. Its aging process (i.e., slaking and storage under water for long periods) has widely been studied as it is important in the preparation of the mortars used in the restoration of historic buildings [5]. It is generally accepted that the longer the lime is stored under water the better its workability, and by extension the final performance of the mortar, due to a change in the crystalline structure of the portlandite ($Ca(OH)_2$) [5,165].

In the 20th century, although several new base materials appeared (especially Portland cement and concrete) and various modern painting techniques (acrylic, vinylic, and silicate-based paints, among others), traditional fresco artists could still be found, such as Gino Severini (1883 – 1966) and his frescoes at Saint-Nicolas de Myre Church (Semsales, Switzerland) [166], or Juan de Aranoa (1901 – 1973) [6], who painted the frescoes in the Zaldibar Hospital chapel (Basque Country, Spain) [167]. Although for a time lime fell into disuse, in recent decades there has been a revival in the use of lime mortars for heritage restoration, as they fulfil the three main requirements of a restoration mortar, which are: chemical-mineralogical and textural compatibility with the traditional building materials, reversibility and durability [127,168]. In this sense, and despite the availability of these other alternative materials, lime mortars could still be recommended today as suitable materials for the preparation of walls for fresco painting.

Nowadays, as pointed out by Nordmark [169], two kinds of aggregates should be used in frescoes: 'bank sand' (i.e., deposits with a low percentage of clay occurring in banks or pits), sharp or smooth-edged, and marble powder, as recommended by other contemporary artists [14,16,82,163]. As regards pigments, prior to the Industrial Revolution (around the 18th century), proper refinement and separation of the raw materials was impossible, which meant that the pigments were very like their geological equivalents [84]. It was not until the end of the 18th century when more efficient methods emerged, and scientists had better tools to deal with the problems traditionally encountered in their disciplines. In this way, the discovery of new chemical elements such as cobalt (Co), chrome (Cr), zinc (Zn) and cadmium (Cd) raised pigment chemistry from a pseudo-scientific alchemy to an exact science [85,170,171]. Scientific progress gave rise in turn to great scientific discoveries. Within the field of pigments, for example, cobalt blue ($CoAl_2O_4$) (1777), Scheele's green ($AsCuHO_3$) (1775) and chrome yellow ($PbCrO_4$) (1778) are worth mentioning [172]. However, in relation with chrome yellow, it should be pointed out that the mineral pigment crocoite ($PbCrO_4$), i.e., natural chrome yellow, was already used during the Middle Ages as it has been found in frescoes beneath the cathedral of Siena (Italy) [173], and in frescoes outside the Mediterranean region (Kuřívody, Czech Republic) [174].

During the 19th century, a series of pigments appeared as substitutes of traditional pigments since they were expensive, toxic or with a questionable permanence [175]. For instance, the use of barium white ($BaSO_4$) began around 1782 as an alternative to the toxic-known lead white [176]. Other white pigments progressively appeared such as zinc white (ZnO) (1834) and titanium white (TiO_2) (1916) [170,177], though the latter is primarily found on frescoes as a part of restoration treatments i.e., chromatic reintegrations. Additionally, due to the high cost of natural ultramarine, a synthetic ultramarine ($3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2Na_2S$) was developed in 1824 as its artificial equivalent [42]. At the time, chemistry was advancing quickly, enabling the development of the well-known 'mars pigments' as equivalents to iron-based pigments (i.e., mars red -Fe_2O_3-, equivalent to hematite) [42,171]. However, even though new pigments were being developed, traditional ones continued to be used like those identified in the fresco by Pasqualoni in the Church of *Saint Nicola* in Carcere, e.g., red ochre, goethite, orpiment, green earth and malachite, together with industrially synthesized pigments, such as artificial ultramarine and chrome green [161]. Additionally, some of the modern pigments such as cadmium yellow (CdS + CdSe) and cobalt blue ($CoO{\cdot}Al_2O_3$) have been found on 20th century frescoes mixed with other pigments [178].

Research and development of pigments continued during the 20th century with the publication of extensive literature on their history, terminology, manufacture, mineralogy, and chemical composition. During recent decades, valuable contributions have been made in textbooks, and scientific reviews have been carried out on the use of lead-based [179], copper-based [108], mercury-based [88] and arsenic-based [180] pigments in art. Nevertheless, since very few fresco murals have been painted over the last century, little is known about whether cobalt, chrome, zinc and cadmium-based pigments are suitable for use in *a fresco* (i.e., due to the alkaline environment of the lime mortars).

Discussion about the discrepancies regarding the standard components of a fresco wall painting

After analysing each of the different treatises and the historical evolution of fresco wall paintings, a series of discrepancies have been observed.

The mortar components

Mortars are heterogeneous building materials composed of an inorganic binder, an aggregate and water, with possible secondary components such as additives and admixtures. It is worth mentioning that the choice of one or another type of binder and aggregate has always been constrained by the local availability of the raw materials, which explains why they had such varied compositions in frescoes.

Lime has been the most used binder for the preparation of frescoes. As it is widely known, lime can be either aerial or hydraulic, depending on its hardening/setting mechanism [19]. On the one hand, *aerial* limes (*air-hardening*) are binders that harden in contact with atmospheric carbon dioxide in the presence of humidity. To obtain aerial lime all authors recommend, subject to local availability, the use of pure limestone which, after calcination and slaking, gives rise to a calcitic lime ($Ca(OH)_2$), also known as *fat lime*. In some cases, dolostones were used as the raw material, thus obtaining a dolomitic or magnesian lime ($Ca(OH)_2$ and $Mg(OH)_2$), also known as *lean lime*. Dolomitic lime was recommended by some authors like Cennini [132] (Table 1), although the presence of periclase (MgO) and brucite ($Mg(OH)_2$) in this type of lime may result in an incomplete carbonation which can have serious consequences related to the drying of the wall painting and its conservation [219]. This has been related to conservation problems observed in *Last Supper* of Leonardo [220]. Even so, dolomitic lime mortars have been found in different periods such as in the Roman city of *Emona* (Ljubljana, Slovenia) [221] or in Roman wall paintings from the archaeological site of *Las Dunas* (Malaga, Spain) [222], in Carolingian frescoes from Saint John's Abbey in Müstair (Switzerland) [223] or in the Byzantine church at the archaeological site of *Anaia* (Turkey) [224].

On the other hand, *hydraulic* binders are those that harden in the presence of high relative humidity or even under water, due to the reaction of the silicates and aluminates present in their composition with water, forming hydrated calcium silicates (C-S-H), aluminates (C-A-H) and hybrid hydrated calcium alumino-silicates (C-A-S-H), the latter being one of the most common phases in ancient mortars [13,225,226]. This binder group is composed of a larger number of binder types compared to the aerial ones. The first hydraulic binder used in the history of construction was during the Neolithic period (10,000 – 2200 BCE) by adding volcanic tuffs and plant ash to the lime [227]. Throughout the Greek and Aegean period (2nd millennium BC), hydraulic mortars were developed by the mixture of aerial lime and volcanic rocks [227,228]. This technology was later successfully improved by the Romans with the use of pozzolana powder (known as *pulvis puteolana* by Vitruvius, a pyroclastic rock powder from the Phlegraean Fields, specifically the city of Pozzuoli in Naples Bay, Italy) and *cocciopesto* (i.e., crushed bricks) [229]. These are reactive materials, rich in amorphous silica (SiO_2) and alumina (Al_2O_3) [226] that, under the alkaline conditions induced by the lime, react with calcium giving place to C-S-H, C-A-H and C-A-S-H. The high cohesive properties and mechanical strengths of these hydraulic mortars justify the extensive use of pozzolan powders, which were widely traded along the provinces and the Mediterranean basin during the Roman Empire [226,230]. However, even though the use of pozzolanic materials (e.g. pyroclastic rocks, volcanic ash, crushed terracotta, plant and animal ashes [229]) was firstly recorded in the literary sources by Vitruvius [74], it has been found in pre-Roman times. For instance, volcanic ashes were identified in different constructions from Ancient Corinth (Greece, 6th – 2nd century BC) [231]. Both pyroclastic rocks precedent from Naples Bay (i.e. *pulvis puteolana*) and other alternative local materials such as ceramic fragments and organic ashes were found in the Punic-Roman city of Nora in Sardinia, Italy (from 2nd BC onwards) [225], showing that Romans not only developed advanced material technologies but probably recovered ancient material traditions [232,233]. Additionally, it is also known that sometimes impure limestones were used for the manufacture of lime, with the consequence that feeble natural hydraulic limes were produced. For example, at the fresco wall paintings from the catacombs of Ptolemy IV at Karnak temples in Luxor, Egypt [234], calcium silicate ($CaSiO_3$) was identified, proving the use of a hydraulic lime.

Regarding the aggregate used for the preparation of frescoes, it is also common to find many different recommendations among the studied sources. Archaeological evidence indicates that siliceous aggregates (e.g., quartz, SiO_2), with different gradings were commonly used for the first layers (*arriccio*), as well as in the final layer (*intonaco*) together, according to some authors, with finely ground marble (Table 1). However, Vitruvius recommended using actual marble only when spatic calcite (*salis micas*) was not available [74,235]. The use of siliceous aggregates has been found in frescoes throughout Europe, from all periods. Examples include medieval frescoes in Sicily (Italy) [128] and Renaissance and Baroque paintings in Granada (Spain) [236]. In some cases, these siliceous aggregates were also accompanied by iron compounds [237] or crushed bricks [238]. Regardless the nature of the aggregate, all the ancient authors agree that the layers should be applied with an aggregate of increasingly fine grain-size. They also coincide on the unsuitability of sea sands, advising against their use, a recommendation that has been followed since ancient times [6,16]. The use of crushed shell has also been recurrent, and even though it has not been referred to by historical treatises (Table 1), Dilaria reports numerous cases in the Mediterranean area dating from the Bronze Age up to the Byzantine period [239].

Finally, the addition of straw is worth mentioning since it seems to have been recurrent during the Medieval Age (Table 1), as observed in numerous scientific studies regarding this period. It is well known that its addition is done aiming to reduce shrinkage during the carbonation process [73]. However, this seemed to have already been known in ancient times as it has been found in stuccoes from Minoan wall paintings [240]. Stefanidou et al. shows that the use of pozzolana, shells or straw in lime mortars has been recurrent in all periods [241]. This is a clear example that craftsmen and artists did not always follow traditional guidelines (treatises or manuals) but rather resorted to the materials most accessible to them and probably based on their own personal experience.

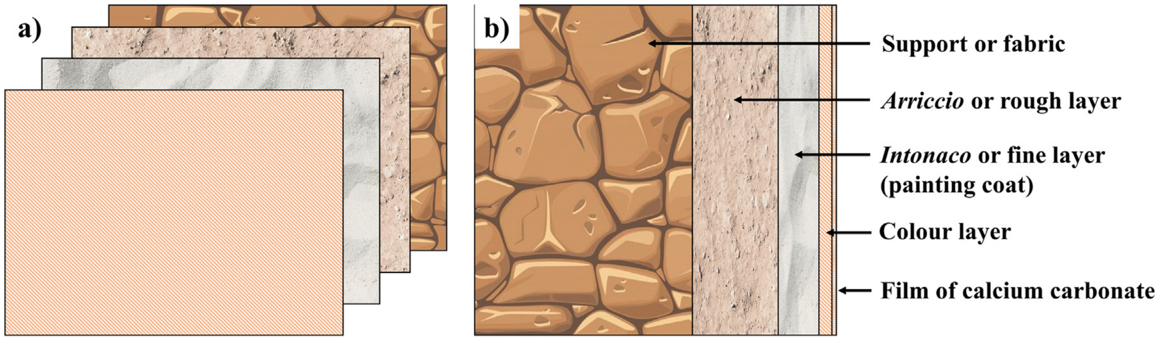

Fig. 1. Most common anatomical structure of a fresco wall painting.

The mortar layers

As regards the ideal number of layers of mortar that a wall painting should have, not only does this vary from one historical period to the other, but also between authors from the same period. For instance, Vitruvius [74] mentions seven layers, whilst Pliny the Elder [69] mentions just five. Authors from the Middle, Modern, and Contemporary Ages also differ within a range of two to four layers (Table 1). The vast amount of archaeological evidence suggests that the number of layers must have depended on many factors. Two layers (*arriccio* and *intonaco*) seems to have been the most common format for fresco base walls, as shown in Fig. 1. There is also some dispute amongst the authors regarding the names given to each of the layers, e.g., *trillissatio, rinzaffo, arenato, arriccio* or *arricciato* for the first rough layers, and *intonaco, intonachino* or *marmorino* for the final layers with smoother finishes.

The composition of each of the layers in terms of their binder-aggregate ratio also varies considerably (Table 1). Whilst some authors recommend that the first layers (*arriccio*) be applied in a 1:3 ratio [14,69,74,147], others prefer 1:2 [132,242]. Similar discrepancies appear with the last layer (*intonaco*), for which some authors recommend 1:2 and others 1:1.

The pigments

Regarding the nature of pigments, inorganic ones are understood to be the most suitable for use in fresco painting (i.e., in an alkaline environment) [7], as demonstrated by extensive archaeological evidence. However, organic pigments such as indigo have been encountered in some fresco wall paintings [7,95], for example in Mesoamerica [243]. Nevertheless, to the best of our knowledge, in the Mediterranean, organic pigments have only been found in Minoan and Mycenaean Greece, where saffron yellow and indigo were used [244], though no organic binder identification has been carried out [254] and therefore *a secco* technique cannot be ruled out.

Since Antiquity, artists were aware that some pigments were sensitive to light and heat when used in murals. For instance, Vitruvius [74] warned about the instability of lead white, Pliny the Elder [69] about cinnabar, and in the Middle Ages, Vasari [145] warned about the lead red in frescoes turning darker. Likewise, authors such as Cennini [132] warned against using pigments that were not resistant to alkalis, such as organic pigments and lead, copper, or mercury-based ones [88,95,108,179]. Despite these warnings, they are still stated to be found in fresco wall paintings (Table 2). Contradictions like these occurred in all historic periods. For this reason, in the following subsections we will discuss discrepancies regarding the use of these "unsuitable" pigments. As no contradictions were found related to the use of earth-based pigments (i.e., green earth or yellow ochre), known to be very stable [245], these pigments have not been dealt in this section.

Another difficulty when discussing pigments is the wide variety of names used. On the one hand, these can vary from the Greek, Latin or Mediaeval names to the modern tradenames [92,113], which must inevitably lead to confusion among artists. On the other hand, we have also encountered that many scientifical studies often used inadequate terminologies for some pigments. For instance, the term *lapis lazuli* is often used to designate natural ultramarine [158,200], when actually lapis lazuli is the mineral from which the pigment is obtained. Another example is the assignment of vermilion without carrying out adequate analysis to differentiate it from its natural equivalent (cinnabar), i.e., through the presence of impurities, the particle size range or morphology [107,189]. Care must therefore be taken when making the assignment of certain pigments and the terminology used.

Copper-based pigments

Copper-based pigments, such as malachite, azurite, verdigris, chrysocolla, etc., were widely used during the Middle Ages in fresco wall paintings (Table 2). It should also be pointed out that other artificially obtained copper salts can also be encountered in wall paintings i.e., copper chlorides or sulphates [108]. Whilst some authors recommended their use [14,69,141], others did not [114,132]. Some, such as Pedrola [242], recommended malachite, but not azurite. It has also been claimed that the exposure of copper pigments to alkali, an intrinsic property of lime-based mortars, caused blackening due to the formation of tenorite (CuO) [108]. In any case, many scientifical studies have stated that many copper-based pigments have been used *a fresco*, such as malachite in the Monastery of Saint Jeremiah (4th century) (Saqqara, Egypt) [112]; azurite in Byzantine wall paintings in the Protaton Church (Mount Athos, Greece) [131] and by many Italian artists such as Cimabue, Giotto, Signorelly and Lorenzetti, among others [110]; or the use of verdigris by Bartolomé Matarana in the Royal College-Seminary of Corpus Christi (Valencia, Spain) [246]. However, it has been seen that some authors like Palomino [150] recommend the use of milk to apply copper-based pigments on frescoes [151], and this should not be easily overlooked. Moreover, it has also been discovered that Giotto used (intentionally or unintentionally) a copper-bismuth arsenate mineral known as mixite ($BiCu_6(AsO_4)_3(OH)_6{\cdot}3H_2O$) [247] as blue pigment. Although it was on panel painting (*Madonna and Child*, National Gallery of Art, Washington DC, USA), it is an indication that painters used pigments that were not found in the traditional palette.

Malachite was known as *chrysocolla* by the Greeks and Romans [69,74,93], and in various mediaeval treatises, thus leading to misinterpretations and confusion [108,109]. The term 'malachite' comes from the Greek *malache*, in reference to its leafy green colour [248], while chrysocolla is nowadays a separate pigment of copper silicate hydroxide hydrate ($(Cu,Al)_4H_4(OH)_8Si_4O_{10}\cdot nH_2O$) [92]. As regards azurite, it was known as Cyprian blue (*caeruleum Cyprium* in Latin, i.e., from Cyprus) [69], although there was also a pigment called *armenium* (i.e., from Armenia), which could have been azurite or lazurite [92]. Egyptian blue, a calcium copper silicate, known in Latin as *caeruleum* [74] or *caeruleum Aegyptium* [69] is also worth mentioning. It had various other names such as Vestorian blue (*Vestorianum*) after Vestorius, a Roman who started producing it in Italy, and whose pigments were described as 'the most refined' by Pliny [69,92]. It was also known variously as Puteolan blue (*Puteolanum*), Pompeii blue or Alexandrian blue [85,92], variably changing its nomenclature depending on its origin.

Lead-based pigments

As for lead-based pigments, whilst Vitruvius [74] recommended the use of lead red (i.e., minium), as found in Roman wall paintings at the *Castulo* archaeological site (Jaen, Spain) [249], no medieval, modern, or contemporary authors considered it suitable for alkaline environments. However, it has been found in several Byzantine churches (Mani Peninsula, Greece) [185]. The same is true of lead white (*cerussa* in Latin), which was used in 15th century frescoes in *Saint Orso Priory palace* (Aosta, Italy) [105], although it is widely known to be unstable under high pH conditions [179]. In a study carried out by Daniilia and Minopoulou, the transformation of lead red (Pb_3O_4) to black PbO_2 was observed regardless of the painting technique (*fresco, fresco-secco* and *secco*) [250]. Therefore, it can be considered that some pigments that are said to be unstable *a fresco* continue being even mixed with organic binders.

As regards names, mercury sulphide known today as cinnabar, was known as *minium* in Latin [69,93], and lead red was known as *minium secundarium* or *cerussa usta* [69,92]. Later, during the Modern Age, the term *minium* was used exclusively to refer to lead red, although previously it had also been used to refer to lead orange and cinnabar pigments, so generating further confusion [42].

Mercury-based pigments

There were also discrepancies regarding mercury-based pigments such as cinnabar/vermilion. On the one hand, even though Vitruvius [74] and Pliny [69] did not recommend the use of cinnabar *a fresco*, it has been found in numerous Roman wall paintings such as the *Domus of Octavius Quartio* in Pompeii (Naples, Italy) [187]or at King Herods Palace from the 1st century AD (Jericho, Palestine) [91]. By contrast, Alberti [141] and Palomino [150] both considered it suitable for fresco wall painting, as found in 15th century frescoes. For instance, cinnabar/vermilion was used in frescoes in Pec Monastery (Ston, Croatia) [216] and in the Monastery of San Isidoro del Campo (Seville, Spain) [188]. As Gliozzo [88] made clear, even though cinnabar had been considered unsuitable for fresco work since ancient times, it was still widely used in the decoration of buildings.

Mixed pigments

To conclude this section, we should also consider the colours produced by mixing different pigments together, a constant feature of wall painting throughout history and action to which the different sources barely refer to. In ancient times, in Cretan frescoes, greens were obtained by mixing Egyptian blue with ochre [251]. Similarly, mixing malachite with Egyptian blue or yellow ochres was a common feature of Pompeian paintings [17,75,90]. Pliny [69] reports that it was also frequent to mix cinnabar with hematite or lead red for economic reasons, and for obtaining specific shades, as seen in Roman frescoes [249]. A similar mixture was found in the 13th century *Peregrina* convent (León, Spain) [217]. He also describes the process for obtaining different shades of brown by mixing hematite and black carbon [249]. This may explain why certain pigments were used even though they were not resistant to alkalis. One example is malachite, which was often mixed with Egyptian blue or ochre to obtain different hues [90].

Later, during the Renaissance, Da Vinci obtained blue-green colours by mixing other earth-compound pigments [252]. Additionally, due to the short supply of suitable green pigments during the 17th century, blue and yellow pigments were commonly mixed to obtain green colours [253], as in the frescoes painted by Palomino in Valencia (Spain), where Naples yellow and blue smalt were mixed [133]. These examples show that mixing pigments to form new colours was common practice throughout history.

Limitations to state the pictorial technique

At this point we must consider that the use of organic binders on wall paintings (i.e., *a secco*) precedes the fresco technique by around 20.000 years, being the oldest form of wall painting [254]. The organic binding materials that can be found is wide-ranging (e.g. egg, milk, glues, resins, gums, etc.) [255] and their identification can be a challenging issue for several reasons: i) their presence is normally very low (<1 mg), ii) several organic and synthetic substances are often present, and iii) non-original compounds can be present as a result of natural decay, pollution or restorations treatments [256], often being difficult to state the pictorial technique (*a fresco, mezzo-fresco, a secco*) [255]. Piovesan et al. state that *a fresco* and *mezzo fresco* techniques can be distinguished by the thickness and the number of calcium-rich painted layers [257]. These features are well observed for instance in the wall paintings from Saint George church in Staro Nagoricino (N Macedonia) where both painting techniques were used and clearly distinguished [258]. Nevertheless, when *a secco* wall painting is studied, often the presence of organic binders is either not always properly identified by analytical techniques or is not found due to natural decay phenomena (e.g., degradation, denaturation, ageing and/or environmental stress) [254]. Therefore, their presence is only found in residual concentrations (around 10% *w/w*) or as degradation products (e.g., oxalates) [254]. This leads to a wrong assignment of the use of some pigments in fresco wall paintings, even though some of them (e.g., copper- or lead-based pigments) are known to be unsuitable under the conditions of high pH of a fresco. Cuní, for example, manifested that some Roman wall paintings have been assumed as frescoes due to the difficulty of identifying organic binders and the lack of results obtained by analytical techniques [87]. He studied various wall painting samples from several archaeological sites in Spain [259] finding that Roman artists had used a water-soluble encaustic paint of beeswax and soap. In other cases, such as the medieval wall paintings in *Santa Maria delle Cerrate* in Puglia, Italy [207], it has been demonstrated that a combination of *a fresco* and *a secco* techniques were used. With this in mind, the assignation made by some authors of the identification of some pigments in fresco wall paintings might not always be completely right whereas a combined painting technique might have been used (i.e., fresco-secco) but had not been properly identified.

Conclusions

In this research, our aim has been to compile all the available information on fresco wall painting, since its appearance in Antiquity to the present day in the Mediterranean region, so as to be able to better appreciate the multitude of variations and contradictions in the fresco technique in terms of the materials used (e.g., pigments) and the execution procedures (e.g., number of layers). Our results show that the constituent materials and technical procedures used in the execution of frescoes varied according to the historical period, the geographical location and accessibility of materials, and the individual artists, not always following what was stated in treatises and art manuals.

Regarding pigments, the identification of mineral pigments different from those mentioned or found in the traditional pictorial palette has been seen as something recurrent (e.g., aerinite, riebeckite or crocoite) and is probably due to the accessibility of each local geographical area. It has also been highlighted here that the identification of the fresco technique in numerous studies is commonly not well supported by a complete analytical study. This is often the case of presumably recognised frescoes where pigments that are unstable under alkaline environment are identified. A common aspect of these studies is the lack of specific chemical analyses to detect possible organic binders remains, which would indicate, instead, *a secco* or a combined fresco-secco technique.

Consent to participate

The authors declare that they agreed to participate in the present review.

Consent for publication

The authors declare that they have read and agree to the publication of this paper.

Author contributions

Daniel Jiménez-Desmond: writing of the original version of this manuscript. José Santiago Pozo-Antonio and Anna Arizzi: revision and proofreading of the manuscript.

Acknowledgements

This study was funded by Research Projects PID2020-119838RA-I00 and ED431F 2022/07. Daniel Jiménez-Desmond was partially financed by the Xunta de Galicia project *Limpeza sostible do patrimonio pictorico: optimizacion dos procesos de ablacion laser* (ED431F 2022/07) and the Spanish Science and Innovation Ministry project RYC2020-028902-I. J.S. Pozo-Antonio was supported by the Spanish Science and Innovation Ministry project RYC2020-028902-I. A. Arizzi was funded by State Research Agency (SRA) and the Ministry of Science and Innovation under the Research Project PID2020-119838RA-I00, within the Junta de Andalucía Research Group RNM179. We also thank Nigel Washington for his review of the original English text. Funding for open access charge: Universidade de Vigo/CISUG.

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