

REVIEW

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On the stability of mediaeval inorganic pigments: a literature review of the effect of climate, material selection, biological activity, analysis and conservation treatments

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Abstract

This review is to be considered part of the development of the MEMORI dosimeter, to evaluate the impact of climate (relative humidity, temperature, illumination, etc., including volatile organic compounds) on moveable objects. In the framework of the MEMORI project, Ghent University was given the task to assess pigment degradation upon acetic acid exposure, and to collect information on pigments' stability. Moreover, to obtain a wider knowledge on the stability of common pigments, the effect of a variety of parameters was reviewed from literature. Discolouration and degradation of pigments significantly alter the legibility of polychrome works of art, so that the development of monitoring methods to ensure the preservation of cultural heritage objects is of primary importance.

Keywords: Pigments, Degradation, Discolouration, Ultramarine, Copper pigments, Smalt, Arsenic sulphide pigments, Vermillion, Lead pigments, MEMORI project

Background

Colour is one of the most important properties of objects, in archaeology and art history. This review is aimed at collecting information on the stability of traditional inorganic mediaeval pigments under a variety of conditions. The pigments considered are whites (lead-white and calcium carbonate), yellows (ochres, orpiment, massicot, lead tin yellows), orange-reds (ochres, realgar, vermillion, litharge, red lead), blues (ultramarine, blue ochre, smalt, azurite, Egyptian blue), greens (green earths, malachite, verdigris and other Cu containing materials), brown (umbers) and black (carbon black). Pigments as Naples yellow ($\text{Pb}_2\text{Sb}_2\text{O}_7/\text{Pb}_3(\text{SbO}_4)_2$), lead chromate yellows ($\text{PbCrO}_4/\text{PbCr}_{1-x}\text{S}_x\text{O}_4$), Prussian blue ($\text{KFe}[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}/\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$), zinc white (ZnO), etc., although known to degrade, are not included in this review, as they were not available during the

Middle Ages [1]. For the purpose of this review, mainly chemical and archaeometrical literature was reviewed, so that an explanation for the on-going degradation processes could be provided as revealed by advanced analytical techniques.

The starting point for such data collection has been the MEMORI project [2], directed at studying and understanding the impact of the air quality inside museum exhibition cases and storage premises on complex objects of cultural relevance. Relevant factors are relative humidity (RH, stable, fluctuating), temperature, illumination conditions, inorganic pollutants, and volatile organic compounds; the latter being extensively studied during the MEMORI project [3, 4]. Moreover, information on the influence of other factors was collected from literature. The results of investigations of works of art are combined, when possible, with specific studies on pigments reactivity performed in the lab using powders or mock-ups. Attention is given to the evolution of the interpretation of specific processes as a result of scientific advancement in understanding the on-going chemical reactions. This review is not limited to the application of

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a specific analytical technique for detecting and understanding degradation processes; on the other hand, it focusses on the so far identified alterations, their impact on the polychromy appearance, and their causes.

Centuries of practical knowledge allowed artists and artisans to select materials which were not susceptible to fading or discolouration, and recommendations on unstable pigment mixtures (therefore not recommended), or on the use of specific pigments with selected binders, are common in artistic literature and treatises (see, for example, Cennini's "Il Libro dell'Arte" [5]). Artists and artisans were anyway constantly experimenting, and the material selection was performed according to their *savoir faire* and to practical considerations [6, 7], often using unstable mixtures during the actual production of the object, which nowadays result in hardly legible works of art. Also, the material history of the polychrome objects, being subjected to the environment, including seasonal climatic changes and extreme conditions such as in fires and floods, to biological activity, and to pollution related to the industrial revolution (sulphur and nitrogen compounds SO_2 , SO_3 , NO_x [8–11]), is bound to provoke alterations on those materials sensitive to climatic factors, to biological activity, and to anthropogenic pollutants. Finally, another important aspect to consider is the human intervention on the objects, which is here reunited under the umbrella term of "conservation treatments". Relevant activities which might alter the stability of pigments in paint layers include, but are not limited to, harsh cleaning procedures and restorations performed by using unsuitable/incompatible materials and methods, or interventions regarding (lack of) climatic control. Finally, also the scientific approach to materials characterization might modify irreversibly the sample during the analysis. It is important to mention that these factors often act in synergy.

The review is articulated in sections corresponding to the main element present in the pigment, according to increasing atomic number. When possible, a general introduction to the sensitivity of the class of pigments is given, with more details for each single pigment. An overview of the observed alterations and the main factors involved in the process (climate, material selection, biological activity, analysis and conservation treatments) is given in Table 1.

Low atomic number (Z) elements

Carbon blacks (C)

Carbon blacks (disordered C) are worldwide commonly used in arts and crafts throughout the centuries [1, 12]. They are of natural or artificial origin, and the microscopical structure of the pigment is related to its origin and manufacture process [13, 14]. They are stable to light

and humidity, but burn at high temperatures. Their curing properties in oil are poor, often requiring the addition of siccatives [12, 15]. Evidence of degradation is observed upon exposure to oxidizing agents, and especially when impurities are present (e.g. presence of residual salts/uncarbonized moieties in carbonaceous pigments applied by using the *fresco* technique) [12, 15, 16]. Whitening is also reported for bone black [amorphous carbon with apatite $\text{Ca}_3(\text{PO}_4)_2$] in oil binding medium, possibly related to the photodegradation of the aromatic structure, probably catalysed by lead (present as a siccative, or pigment) [17]. In another study, by the same authors, a variety of issues was identified related to the causes of discolouration of carbon blacks, such as the formation of lead carboxylates from the reaction of the siccative with the binder, or the alteration of lakes present in the mixture, or the degradation of the aromatic carbon compounds. The latter process is related to both the manufacturing process of the carbon based pigment, and the presence of siccatives [15]. Upon infrared laser irradiation, the colour of mock-ups prepared with organic and inorganic binders changed, showing evidence of darkening [18], while a 248 nm (UV) laser induced no changes [19].

Ultramarine blue ($\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_n$)

The term lazurite refers to the blue mineral of the sodalite group ($\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_n$), lapis lazuli to the rock from which it is extracted. Notwithstanding its enormous price related to its rarity and colour, natural ultramarine was extensively used throughout history, as a decorative stone [1, 20], as a colourant for ceramics [21–23], and in paintings and manuscripts both in Asia and Europe starting from the 6th century [24], as well as in pre-Columbian cultures [25]. In European contexts, this extremely valuable material was mined in present-day Afghanistan and traded via Venice [1, 20], and it was reserved to specific iconographic elements of the composition, such as Christ and the Virgin's blue cloaks [1, 20, 26, 27]. It was used both in tempera and oil, to produce either mixtures (with crimson or a white pigment for example) or pure layers, of different opacity according to the binder (e.g. oil based blue glazes painted over a cheaper blue layer [1, 26]). The high price and marvellous colour somehow promoted the development of adulterations, and finally the synthesis of artificial ultramarine in 1828 by Guimet, and in the same year, but with a different process, by Gmelin [1, 20, 28]. Natural ultramarine is stable to light, including lasers [18, 29], heat, acids and alkalis [20, 30, 31]. No oxalates were formed upon exposure of the pigment to oxalic acid [32]. It was however observed that in presence of SO_2 (pollution), the pigment discolours only when liquid water (e.g.

Table 1 Summary of the observed discolourations on traditional inorganic mediaeval pigments

Colour	Pigment	Climate effect	Fluatuating RH	RH + chlorides (Cl ⁻)	RH + pollutants (SO ₂ , SO ₃ , NO _x)	RH + salts	Oxidizing agents	Alkali	Acids	Hydrogen sulphide (H ₂ S)
White	Calcium carbonates CaCO₃	Swelling of paint layers [20, 45]	Swelling of paint layers, mechanical stress		Formation of gypsum, mechanical stress (increased volume), lixiviation of soluble material [20, 45, 46]				Decomposition [32, 50, 53, 54]	- [45]
White	Lead white 2PbCO₃·Pb(OH)₂	Blackening on wall paintings, watercolours and manuscripts [20, 60, 231]. Synergistic effects with the other parameters			Blackening [9, 64, 124, 166]	Formation of various salts, sometimes not white [56, 123, 218]. Cerussite is the most stable	Blackening [213]	Blackening [213]	Soluble [20, 98, 229]. Formation of oxalates [32, 56] and acetates [109] upon exposure to oxalic and acetic acid respectively	Blackening (especially manuscripts and watercolours, [9, 20, 60, 98, 190, 191, 200, 204, 211–213, 231, 232]). Formed PbS can be converted to PbSO ₄ [139, 212], and finally cerussite/hydrocerussite again
Yellow	Orpiment As₂S₃	Dissolution. Formation and transport of As ⁵⁺ ions [180, 183]. Whitening (formation of As ₂ O ₃) in presence of light [64] and of oxidizing conditions [9, 176]					Whitening (formation of As ₂ O ₃) [9, 20]	Soluble. Not recommended for wall paintings [123, 176]	Soluble	
Yellow	Massicot PbO	Initial darkening, then degradation to cerussite/hydrocerussite [64]			Initial darkening, then degradation to cerussite/hydrocerussite [123, 218]					Formation of black PbS [124]

Table 1 continued

Colour	Pigment	Climate effect									
		High RH	Fluctuating RH	RH + chlorides (Cl ⁻)	RH + pollutants (SO ₂ , SO ₃ , NO _x)	RH + salts	Oxidizing agents	Alkali	Acids	Hydrogen sulphide (H ₂ S)	
Yellow	Lead tin yellow Type I: Pb₂SnO₄ Type II: PbSn_{1-x}Si_xO₃	- [64]								Formation of acetates [109] and carboxylates [56, 225, 247]	Formation of PbS [246]
Yellow, red, brown	Yellow, red, brown ochres Fe₂O₃ , FeOOH , Fe₃O₄ , Mn_xO_y	Hydration of oxides [red to yellow, 53]			Hydration of oxides, formation of hydrated sulphates [73]					- [1]	-, formation of Ca oxalates from the other minerals in the ochre [32, 67]
Orange-red/yellow	Realgar/pararealgar As₄S₄	Formation and transport of As ⁵⁺ ions. Whitening (formation of As ₂ O ₃) [180, 183]									
Orange	Litharge PbO				Degradation to cerussite/hydrocerussite, sulphate and phosphates [218]	Degradation to cerussite/hydrocerussite, sulphate and phosphates [218, 236]					
Red	Vermillion HgS	Unstable. Synergy with photodegradation and oxidation [64, 66]	Involved in discoloration and sulfation [106, 197, 199, 202, 203, 207-209]							Unstable [103, 123, 200], but still used in wall paintings [73, 193, 201-203]	
Red	Red lead Pb₃O₄	Unstable, blackening upon light exposure [1, 64]	Involved in discoloration [93, 245]		Whitening [68, 93, 200, 228, 237, 238]	Discoloration, as lead salts are most of the time white/whitish [68, 93, 123, 200, 218, 228, 237, 238, 244]				Unstable [1, 120]. Formation of black PbO ₂ and PbSO ₄ in a sulphation process [237, 242]	Sensitive: formation of PbS [1, 60, 93, 124, 238, 241] or PbSO ₄ [59, 68, 233, 242]

Table 1 continued

Colour	Pigment	Climate effect		Fluctuating RH	RH + chlorides (Cl ⁻)	RH + pollutants (SO ₂ , SO ₃ , NO _x)	RH + salts	Oxidizing agents	Alkali	Acids	Hydrogen sulphide (H ₂ S)
		High RH	Low RH								
Green	Green earths glauconite (K,Na)(Fe ³⁺ ,Al,Mg) ₂ (Si,Al) ₄ O ₁₀ (OH) ₂ Celadonite (K(Al,Fe ³⁺), (Fe ²⁺ ,Mg)) (AlSi ₃ ,Si ₄)O ₁₀ (OH) ₂	Discolouration of oil layers [75]							Soluble [74]	Soluble [74]	
Green	Malachite Cu CO ₃ ·Cu(OH) ₂	Recrystallization [111]	Recrystallization [111]	Reaction without colour change [53, 119, 127, 129]	Reaction without colour change [53, 103, 119, 121, 123, 126–128]	Reaction without colour change [53, 103, 119, 121, 123, 126–129]	Reaction without colour change [53, 103, 119, 121, 123, 126–129]		Discolouration [black, 126]	Decomposition [13–138], further reaction of Cu ²⁺ ions [126]	Bluish discolouration on pure pigment; selective attack on other pigments in the mixture if H ₂ S is of biological origin [124, 126, 139]
Green	Verdigris xCu (CH ₃ COO) ₂ · yCu (OH) ₂ · zH ₂ O	Hydrolysis of the organic moieties [133, 147]					Formation of Cu salts [119, 123, 133, 146]	Browning [peroxide species, 146]	Formation of blue copper hydroxides [20]	Formation of oxalates [32]	Bluish discolouration on pure pigment [20, 124]
Green	Copper resinates copper salts of abietic acid								Darkening [132]		
Green	Cu chlorides Cu ₂ Cl(OH) ₃	Polymorphism [115, 119, 121, 158, 160, 165–167]	Polymorphism [115, 119, 121, 158, 160, 165–167]		Polymorphism [115, 119, 121, 158, 160, 165–167]	Formation of Cu salts [167]	Formation of Cu salts [119, 123, 133, 146]		Formation of (unstable) blue Cu(OH) ₂ [115]	Oxalates [127]	
Green	Cu sulphates Cu SO ₄ · yCu (OH) ₂ · zH ₂ O	Polymorphism [127, 129, 168]	Polymorphism [127, 129, 168]	Polymorphism [129, 168]	Polymorphism [127, 129, 168]	Formation of Cu salts [127, 129, 168]				Oxalates [127]	
Blue	Ultramarine Na ₈ [Al ₆ Si ₆ O ₂₄]S _n			Discolouration [grey, 9]					Stable [20, 30, 31]. Discolouration [grey, 31, 35, 36, 38, 39]	Stable [20, 30, 31]. Discolouration [grey, 31, 35, 36, 38, 39]	

Table 1 continued

Colour	Pigment	Climate effect									
		High RH	Fluctuating RH	RH + chlorides (Cl ⁻)	RH + pollutants (SO ₂ , SO ₃ , NO _x)	RH + salts	Oxidizing agents	Alkali	Acids	Hydrogen sulphide (H ₂ S)	
Blue	Vivianite Fe₃(PO₄)₂·8H₂O						Discolouration to green, and finally to yellow [1, 76, 82, 83]				
Blue	Smalt CoO·nSiO₂	Glass alteration, ions leaching and discolouration [89, 91, 96]			In tempera: discolouration (dosimetry, 102). No synergy of SO ₂ and NO _x [87]			Glass alteration [34, 35, 47, 89, 90, 95–97]			
Blue	Azurite 2CuCO₃·Cu(OH)₂	Discolouration [64, 112]	–	Discolouration: black, green [103, 116, 118–121]	–	Discolouration (green, [28, 64, 111, 112, 115–118])		Discolouration: green [91, 114, 119], black [20, 35, 64, 68, 91, 103, 111, 113, 114, 121–123]	Decomposition, further reaction [32, 55, 59, 116]	Bluish discolouration on pure pigment; selective attack on other pigments in the mixture if H ₂ S is of biological origin [111, 124]	
Blue	Egyptian blue CaCuSi₄O₁₀	Green discolouration [156–158]				Green discolouration [156–158]		– [28]	– [28]		
Black	Carbon black C						Alteration, especially if impurities are present [12, 15, 16]	Alteration, especially if impurities are present [12, 15, 16]			
Colour	Pigment	Biological activity, material selection			Light, heat, chemical analyses						
		Biological attack	Binders	Other pigments/additives	Light	Laser/ion beams	High temperature				
White	Calcium carbonates CaCO₃	Formation of oxalates [52, 54]	Formation of oxalates [54], proteinates [51], carboxylates [55–60]	Reacts with verdigris [50]. Cu ions catalyse degradation of binders and formation of oxalates [57, 60]	– [45]	–/discolouration [61]	Decomposition to CaO and CO ₂				

Table 1 continued

Colour	Pigment	Biological activity, material selection		Light, heat, chemical analyses		
		Biological attack	Binders	Other pigments/additives	Light	Laser/ion beams
White	Lead white $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$	Oxalates [32, 56]	Drying properties [230]. Formation of soaps which increase layer transparency [55, 67, 226]	Blackens when mixed with red lead. Reaction with S containing pigments not clear [191, 229]	Influence of the binding medium [70, 142, 150, 210, 215, 233–235]. Formation of massicot-like degradation [72] / discolouration [70, 234]. [151]	Discolouration [formation of massicot, litharge, red lead, 229]
Yellow	Orpiment As_2S_3	Different stability in oil/water based mediums [184]. Unstable in oil [170]	Reacts with verdigris and lead white [1, 30, 170]. As^{5+} deposit around Fe/Mn particles [30, 50, 176]. Formation of As_2O_3 and H_2S [9, 176]	Sensitive, especially to green [20, 30, 128, 177–179, 182, 185, 186]. Synergy with relative humidity	Green lasers [174, 177, 180–182]	Darkening, and then whitening (formation of As_2O_3 and SO_2) [9, 20]
Yellow	Massicot PbO			–	Irreversible darkening, or whitening [150, 215]	Discolouration [formation of red lead, 229] Decomposition at 900 °C [20, 245, 246]
Yellow	Lead tin yellow Type I: Pb_2SnO_6 Type II: $\text{Pb}_5\text{Sn}_{1-x}\text{S}_x\text{O}_{13}$	Drying properties [246]. Formation of lead soaps [56, 225, 247]	–	–	Dehydration of hydroxides/oxihydroxides (yellow to red); modification of the Mn phases (darkening, [18, 19, 29, 62, 63, 69–72])	Dehydration of hydroxides/oxihydroxides; modification of the Mn phases [darkening, 1, 12, 68]
Yellow, red, brown	Yellow, red, brown ochres Fe_2O_3 , FeOOH , Fe_3O_4 , Mn_xO_y	Ca oxalates [from the other minerals, 32, 67]	Fe promotes photo-oxidation, Mn curing of the oil [12]. Reaction products with proteinaceous binder [51, 65]	– [1, 12, 64]. If impurities are present, unstable [12, 66]	Green lasers [30, 106, 177, 180, 181, 188]	Temporary darkening/Whitening (formation of As_2O_3) [20, 189]
Orange-red/yellow	Realgar/pararealgar As_4S_4	Different stability in oil/water based mediums [177, 184]	Reacts with verdigris and lead white [30, 50, 176]. As^{5+} deposit around Fe/Mn particles [180, 183]. Formation of As_2O_3 and H_2S [9, 176]	Sensitive, especially to green [30, 106, 177, 180, 181, 188]	Stable [215, 233], but massicot can be formed [215]	Discolouration (formation of massicot, red lead, 229)
Orange	Litharge PbO	Very reactive towards organic binders, commonly used as dryer [1]. Soaps formation [55]				

Table 1 continued

Colour	Pigment	Biological activity, material selection		Light, heat, chemical analyses			
		Biological attack	Binders	Other pigments/additives	Light	Laser/ion beams	High temperature
Red	Vermillion HgS	- [56]	Protect vermilion from light and from external chloride sources [19, 65, 121, 139, 193, 194, 198, 199, 202, 205, 206, 210]. Watercolour medium offers little to no protection. No oxalates [56]	Mixtures with lead white, minium, and other pigments show increased stability of vermilion [19, 20, 193, 199, 204]. Reactivity with some materials [65, 198, 205]	Blackening, related to halogen impurities [70, 141, 142, 150, 199, 202, 206, 207]	Blackening, related to halogen impurities [70, 141, 142, 150, 206]	
Red	Red lead Pb₃O₄	PbO ₂ can result from biological activity [217, 238, 239]	Protect the pigment from light and humidity [239]. Lead soaps, lead hydroxide, lead acetates and finally lead carbonates are formed [240]	Sensitive to S containing pigment (arsenic sulphides, vermilion and ultramarine, [1, 60, 93, 124, 186, 238, 241]); formation of dark PbS and white PbSO ₄ and Pb arsenate species [241]. It promotes lead white blackening [204]	Affects lean layers of water soluble paint. Both blackening (PbS) and lightening (PbSO ₄ , PbCO ₃) occur. Related to pigment's composition. [1, 5, 59, 64, 93, 120, 238, 240, 243]	Grey to brown discoloration, related to pigments composition. Formation of PbO (which can be re-oxidised to minium, [142]) [215, 240]	Formation of litharge [1, 240]
Green	Green earths glauconite (K/Na) (Fe³⁺, Al/Mg)₂(Si₄Al₄O₁₀(OH)₂ celadonite (K(Al ³⁺), (Fe²⁺, Mg)) (AlSi ₃ Si ₄) O ₁₀ (OH) ₂						
Green	Malachite CuCO₃·Cu(OH)₂	Cu acts as a biocide [124]. Acidic conditions [53]	Organometallic compounds (oxalates, carboxylates, resins, acetates, etc.) [32, 53, 55, 109, 122, 126, 129–135]		-	Discolouration (black, [139, 141, 142])	Discolouration (black, [1, 91, 103, 121, 125, 139, 140])
Green	Verdigris xCu(CH₃COO)₂·yCu(OH)₂·zH₂O		Promotes drying [20, 133, 134, 146–148]; formation of soaps and metalloproteins [35, 50, 67, 133, 145, 147]	The acidic conditions, presence of Cu, light and pollution are involved in cellulose degradation [20]. Darkening when mixed with orpiment or lead white [50]	Browning, darkening (release of Cu ⁺) [146]	-/discolouration [141, 142, 149, 150]	PIXE [151]

Table 1 continued

Colour	Pigment	Biological activity, material selection		Light, heat, chemical analyses			
		Biological attack	Binders	Other pigments/additives	Light	Laser/ion beams	High temperature
Green	Copper resinolate copper salts of abiestic acid		Formation of carboxylates, metalloproteins. Photooxidative processes occur [147, 151]		Darkening [20, 98, 132, 147]	-/-darkening (reduction of Cu ²⁺ to Cu ⁺ , [151])	X-rays [151]
Green	Cu chlorides Cu₂Cl(OH)₃						
Green	Cu sulphates CuSO₄·yCu(OH)₂·zH₂O	Formation of Cu salts [127, 129, 168]					
Blue	Ultramarine Na₈(Al₆Si₆O₂₄)_{5-n}		Catalytic effect of the pigment on binders hydrolysis [41, 42]	Pb neutralizes the acidity of the binder [35]	- [18, 29]		Discolouration [grey, 31, 38, 39] stable [18, 29]
Blue	Vivianite Fe₃(PO₄)₂·8H₂O		Protect the pigment from degradation [47]				Decomposition with discolouration [84, 85]
Blue	Smalt CoO·nSiO₂		Leaching of ions, changes in Co coordination and formation of soaps (grey, blanching, [34, 35, 47, 89, 90, 93–96, 98–101])	Ca neutralizes the acidity of the binder [47, 89, 90, 96], Pb more reactive than K to form soaps [34, 90, 96, 97]			Further discolouration of degraded particles [103]
Blue	Azurite 2CuCO₃·Cu(OH)₂	Cu acts as a biocide [124]	Discolouration of small particles [35]; formation of bluish verdigris (with humidity, [64]); formation of Cu proteinates in tempera [51, 112]; yellowing of binders [111]		- [111, 112]	Discolouration (black, [112, 114, 125])	Discolouration (black, [20, 68, 69, 91, 103, 112–114, 121–123, 125])
Blue	Egyptian blue CaCuSi₄O₁₀		Darkening in gum [155]		-		
Black	Carbon black C		Darkening upon infrared laser exposure [18]	Pb ⁺ driers: white discolouration [17]	Photodegradation of the aromatic structure catalysed by lead [17]	Stable to 248 nm laser [19]	Burning [13]

For each pigment, the chemical formula is given, and the element of interest marked in bold. For each observed alteration, its cause is given, including climate (RH = relative humidity); biological activity and material selection; and light, heat, chemical analyses. If the pigment is reported in literature to be stable to a specific parameter, the symbol “-” is used. If the corresponding cell is left blank, no information could be retrieved from published works

condensation) is present [9]. The sulphur present in the crystalline matrix of lazurite does not affect pigments that are otherwise sensitive to hydrogen sulphide (H_2S), such as leadwhite [20]. No alteration could be observed on decorative plasterworks in the Alhambra (Spain) [33], neither on manuscripts [24]. However, a greyish alteration of the paint surface (“ultramarine sickness”) can be sometimes detected, but it seems that many factors can cause discolouration of lazurite paint layers, such as the oil degradation in presence of humidity [20], or the discolouration of smalt in case of mixtures [20, 34]. It is reported in literature that ultramarine sickness is related to an acidic attack of the pigment by pollutants, biological metabolites, or even acidity of the binder [35, 36]. This hypothesis seems to be confirmed by the fact that, in oil medium, when the basic pigment leadwhite was added to the mixture (to enhance curing, increase opacity and adjust the shade), no visible alteration can be detected, the leadwhite somehow protecting the other pigment [35]. The zeolitic structure of the mineral allows for ion exchanges [20], and for trapping volatile molecules, such as the S_3^- chromophore [37], and CO_2 whose presence was recently related to natural ultramarine from Afghanistan [38]. Artificial ultramarine discolouration revealed a variation in the aluminium coordination, resulting in the opening of the cage and release of the chromophore [31, 39, 40]. Such a cage-opening process can be initiated either by high temperatures, acids [31, 38, 39] or alkalis [31]. Moreover, as known for sulphur-saturated zeolites [41], it appears that ultramarine can have a catalytic effect on the binder breakdown, and that such property can be related to a pigment pre-treatment (heating), which can explain the inconsistent appearance of degradation [42].

Calcium (Z = 20)

Calcium containing pigments are of mineral, biogenic, fossil or artificial origin, mainly corresponding to groups of carbonates, sulphates, phosphates, or fluorides [1]. A variety of Ca, CaMg carbonates, and sulphates was used as white pigment (chalk, *bianco di San Giovanni*: CaCO_3 ; huntite: $\text{CaMg}_3(\text{CO}_3)_4$ and dolomite: $\text{CaMg}(\text{CO}_3)_2$; gypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), as well as mixed with glue to prepare ground layers in northern and southern Europe, respectively [1, 20, 43–45] and to prepare parchment for manuscripts [46]. The calcination of bones gives a white pigment mainly containing apatite $\text{Ca}_3(\text{PO}_4)_2$ [1]. Calcium compounds were as well used as extenders (for example with leadwhite, to achieve transparency effects), and for lakes, as chemical or physical supports [20, 47]. The purple mineral fluorite (CaF_2) was also used as a pigment, mainly in fifteenth to sixteenth century central European artworks [1, 48, 49].

Chalk pigments [(Ca,Mg)CO₃: natural/artificial, lime white, shell white]

Calcite (CaCO_3) can be considered stable under normal circumstances. It decomposes to lime (CaO) and CO_2 when heated, and it is dissolved by acids with release of CO_2 and formation of the corresponding salt. SO_2 pollution is responsible for the formation of gypsum, which is soluble and produces mechanical stress, as its volume is larger than that of the starting material [20, 45]. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is a common degradation product in wall paintings and manuscripts [46]. Being alkaline, these pigments are not suitable for mixing with pigments such as verdigris [50], but they are stable to sulphide containing materials (pollutants or pigments) [45]. The lists of occurrences reported by [45] and [20] mainly refer to calcite containing ground layers, although the use as a pigment is ascertained. Calcium carbonate pigments are not suitable for use in oil medium, as they don't have hiding power [45], but they are used in mixtures with other white pigments to adjust the shade and hue, as well as in wall paintings [7]. In proteinaceous binder, interactions are reported between pigment and medium [51].

Huntite and dolomite, Mg-rich carbonates having formula $\text{CaMg}_3(\text{CO}_3)_4$ and $\text{CaMg}(\text{CO}_3)_2$, respectively, are also identified as white pigments in rock art paintings. As many other carbonatic materials, they are converted to Ca-oxalates (weddelite $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and whewellite $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) in presence of oxalic acid, with the excess magnesium being included in dolomite and magnesite MgCO_3 (which can be considered as intermediate degradation products, sensitive to oxalic acid), in the very soluble magnesium oxalates $\text{MgC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, and finally lixiviated [52]. The attack from polluted water can as well form gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and the extremely soluble magnesium sulphate MgSO_4 , and calcite. The adsorption of water negatively affects the stability of paint layers, as swelling occurs [52].

The use of a *buon fresco* technique implies the use of $\text{Ca}(\text{OH})_2$ as a binder, which recrystallizes into calcium carbonate, surrounding the pigments and binding them to the wall surface. The formed calcite is subjected to degradation processes involving acids, from biological activity or binders degradation (when details are added *a secco*) [32, 53]. Carboxylic acids from binding media are expected [54]. However, these compounds were not always detected in samples [55]. On the other hand, Carboxylates were successfully identified at the boundary between the ground layer and the paint in egg tempera samples [56, 57]. They were as well detected on artworks (laboratory and in situ), especially underneath the varnish and on top of the ground layers [58, 59], and on manuscript samples. There, a correlation between calcium oxalates and the loss of the proteinaceous signal

in green areas was highlighted, so that the binder's degradation is catalysed by Cu-ions, present in the green pigment, and oxalic acid is released [57, 60]. Chalk is lightfast [45], and gypsum does not show discolouration upon Nd:YAG laser irradiation [18]. Ion beam analysis proved to be potentially harmful to chalk, as discolouration was observed [61].

Iron (Z = 26)

Yellow, red, brown ochres (Fe₂O₃, FeOOH, Fe₃O₄; Mn_xO_y)

Ochres are natural products related to rock weathering, whose predominant phases are phyllosilicates (clays). The presence of less than 2% chromophores, such as iron oxides and hydroxides, the red haematite (α -Fe₂O₃) and yellow goethite and lepidocrocite (α -FeOOH and γ -FeOOH respectively), is sufficient to impart a deep colour to the rock [1, 12]. Other minerals are commonly present and can help to ascertain provenance and paragenesis, such as quartz (SiO₂), feldspars ((Na, K)AlSi₃O₈), micas and clays (complex hydrosilicates), gypsum (CaSO₄·2H₂O), ferrihydrite Fe₁₀O₁₄(OH)₂, maghemite (γ -Fe₂O₃) and magnetite (Fe₃O₄), iron sulphates [jarosite group, KFe₃³⁺(SO₄)₂(OH)₆], etc. [1, 12]. If manganese oxides (MnO, MnO₂, Mn₃O₄) are present together with the iron oxides, the shade of the ochre is darker and suitable for producing various shades of brown (Siennas and umbers), and for shadow rendering [1, 12]. The shade of iron oxides and oxi-hydroxides can be adjusted by roasting processes, which produce darker shades (yellow to red-brown; red to purple-dark red) [1, 12]. In fact, haematite, the anhydrous oxide, is the most stable, being the end product of heating goethite and lepidocrocite (150–400 °C); and maghemite (γ -Fe₂O₃) can also be produced if organic matter is present [12]. The transformation of magnetite (Fe₃O₄) to haematite is also reported [62, 63]. These materials are very stable and maintain their colour when ground to powders, moreover their occurrences are numerous: diffusion, stability, lightfastness and inertness make their use as pigments straightforward [1, 12, 64]. In oil layers, Fe-ions promote photo-oxidative reactions, while Mn-ions act as a siccative [12]. In proteinaceous binder, interactions are reported between pigment and medium [51]. In rabbit skin glue, haematite shows a high degree of interaction with the binder, making the paint layer more stable than for other pigments [65]. The instability to light reported for some umbers [66] seems to be attributable to the presence of tarry materials and other impurities [12]. As for the red and yellow ochres, burning produces a darker shade (burnt umber, burnt Sienna) [1]. Ochres are stable to light, moisture, alkali, and dilute acids, and are inert in mixtures. Their stability to acids is testified upon oxalic acid exposure, which causes only the formation of

Ca-oxalates, from the other components of the ochre [32, 67]. They are, however, sensitive to high temperatures, such as fires [12, 68], or local heating effects related to the use of lasers for cleaning [19, 69, 70] or for spectroscopical analysis (i.e. Raman spectroscopy, [62, 63, 71, 72]). A UV (248 nm) laser showed darkening of yellow ochre and raw Sienna, as a result of dehydration, conversion to haematite and modification of the manganese phases present [69], but low fluences of the same laser caused little modification of this ochre [19]. High fluence of 355 and 633 nm laser, caused the conversion of yellow ochre to haematite [29, 72]. The effect of NIR laser irradiation (1064 nm) was as well investigated, showing significant discolouration of both yellow and red ochres when mixed with gypsum (no organic binder) [18], and an increase of haematite content after irradiation of ochres [70]. Moreover, some issues are encountered on wall paintings. In fact, coquimbite/paracoquimbite Fe₂(SO₄)₃·9(H₂O) were identified in Pompeii, together with magnetite Fe₃O₄ and gypsum CaSO₄·2H₂O, as a result of the degradation of the fresco paint layer due to SO₂ pollution [73]. On wall paintings in the Tournai Cathedral, on the other hand, anhydrous haematite was found to be converted to iron oxy-hydroxides due to the humid conditions, which resulted in a visible discolouration of some red areas [53].

Green earths (Fe, Mn, Al, K-containing hydrosilicates)

The green coloured iron-containing silicates glauconite ((K,Na)(Fe³⁺,Al,Mg)₂(Si,Al)₄O₁₀(OH)₂) and celadonite (K[(Al,Fe³⁺),(Fe²⁺,Mg)](AlSi₃,Si₄)O₁₀(OH)₂) can be found in outcrops all over the world [1, 74]. After crushing and grinding, the material is ready to use as a pigment, showing good stability and lightfastness in all media, although in oil the hiding power is relatively poor [1, 74]. Both these characteristics supported the wide use of such pigments. Green earths are soluble in both acids and alkalis, and they turn brown upon heating, as divalent iron is oxidised to its trivalent counterpart [74]. They were as well used as lake substrates [74]. Green earth oil layers exposed to humidity and heat showed discolouration, pinpointing differences based on the binder composition, and ageing conditions [75].

Vivianite (Fe₃(PO₄)₂·8H₂O, blue)

Vivianite is an hydrated iron phosphate. Its blue colour arises from intervalency charge transfer between Fe²⁺/Fe³⁺ [1, 37], as a consequence of oxidation of some of the Fe²⁺ in colourless vivianite [47]. Occurrences of vivianite deposits and of its use as pigment are listed in literature [1, 47, 76–80]. As a pigment, it only shows medium stability [47, 81]. The discolouration of this blue monoclinic phosphate to a greenish hue is attributed either to unbalanced Fe²⁺/Fe³⁺ ratio, or to its oxidation to green

triclinic metavivianite $\text{Fe}_3(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ [1], and finally to yellowish brown amorphous santabarbarite $\text{Fe}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$ [76, 82, 83]. Oxidation is expected to be faster in air, and to slow down once the pigment is embedded in a binder [47]. On top of these oxidation reactions, heat related damages can be observed starting already at 70 °C, causing colour changes in both pure vivianite [84] and oil paint layers containing it [85]. The degradation seems to preferentially affect larger grains [85].

Cobalt (Z = 27)

Smalt (CoO·nSiO₂, blue)

Smalt is a synthetic cobalt-doped potash glass. More details on smalt fabrication and (early) occurrences are given elsewhere [1, 20, 86–88]. It was not only used as a pigment, but as an additive to improve oil curing as well [34, 47, 86]. Coarse grinding of the blue glass was required in order to obtain a satisfactory colour, which seems to have affected the degree of alteration [34, 89]. The discolouration of smalt can be observed in 25–50 years, and it can be related to various phenomena: on one hand, the similarity of optical properties (refraction index) of the glass and of the oil, on the other the instability of potassium glass, Co and K ions being the two species considered as responsible [1, 20, 34, 90]. In fact, smalt use is recommended in wall paintings (*secco* technique) and in aqueous media only [86]. Environmental moisture proved harmful to oil paint layers, to potash glasses [89], and to wall paintings [91]. The first theories on the cause of smalt discolouration in oil assume the role of Co as a catalyst in the binder's oxidation, with the formation of an organometallic compound at the grain boundary [34, 92]. Moreover, a change in cobalt coordination occurs and it is attributed to the oxidation of cobalt [92]. Later studies [89, 93, 94], however, demonstrated that the distribution of potassium in degraded particles of smalt is not homogeneous, while cobalt is confined to the particles, and that K ions are leached out of the glass affecting its K:Co ratio, the pH, and the Co(II) coordination, which result in colour change. As a consequence of K⁺ leaching, the coordination of Co²⁺ changes from tetrahedral to octahedral (X-ray absorption spectroscopy studies (XAS) [90, 94], vibrational spectroscopies and elemental analysis [95]), causing the colour loss; simultaneously, the glass network is modified as the Q³ component related to alkali content decreases, and hydration is observed [95]. The change in pH might additionally damage the glass network. The leached K⁺ ions interact with the aged oil, increasing its water sensitivity, forming soaps and causing blanching [35, 47, 89, 95, 96]. The paint composition might affect the discolouration, by providing chemical species to buffer the potassium leaching. If calcium is present in the glass network,

the pigment appears to be less sensitive [47, 89, 90, 96]. When smalt is mixed with leadwhite in oil, lower degrees of alterations are observed, probably because lead soaps are favoured compared to the potassium ones, so that leaching of alkali is not as relevant as in pure smalt paint layers [34, 90, 96, 97]. The discolouration of smalt and the rough surface of degraded particles significantly alter the appearance of oil paintings where it was used for the sky, or other parts intended to be bright blue [34, 89, 94, 96, 98–101]. Smalt egg tempera samples proved sensitive to environmental conditions in museums, so that such a paint layer might be successfully used as a dosimeter to evaluate the air quality in terms of conservation issues [102]. In glue binder, the role of humidity and airborne pollutants in accelerating glassy pigments degradation was demonstrated, where leaching of both potassium and cobalt ions occurred. No evident effect of SO₂ and NO_x synergy was observed though [87]. In *fresco* wall paintings, smalt is expected to deteriorate due to the very alkaline conditions, to the presence of liquid water (including condensation, capillary rise and infiltrations), to the small particle size increasing the surface reaction, and to the possible contamination by pollutants. Again, leaching of alkali is observed, and in some strongly degraded smalt particles showing cracks, cobalt and other divalent ions are leached as well, probably due to aggressive environmental conditions (humidity, basic pH) [88, 91, 96]. On top of ions lixiviation and weathering of the glass, examples of heat degraded smalt are reported in wall paintings affected by fire [103].

Copper (Z = 29)

It was recently observed that historical copper-based pigments are not only limited to malachite, azurite, verdigris and copper resinate. In fact a variety of salts (organic acids salts such as copper citrate [104], silicates, phosphates, sulphates, chlorides, etc.) were as well used as pigments [105, 106], and should not be regarded anymore as degradation products only. Moreover, the situation is complicated by inconsistent nomenclature use in artistic literature [1, 105]. It is well known that malachite and azurite are not stable in *fresco*, and that they tend to discolour in oil [50]. Studies on metallic copper exposed to a museum-like environment demonstrated its sensitivity to organic acids, including from the binder, so that Cu(II) compounds are always formed [107–110]. More details on the reactivity of copper salts in acidic conditions are given for each pigment in the next sections.

Azurite (2CuCO₃·Cu(OH)₂, blue)

Azurite (2CuCO₃·Cu(OH)₂) was the most diffused blue pigment during Middle Ages, and before [1, 20]. It appears to be stable to light and atmosphere, and

shows good performances both in oil and tempera mediums [111, 112], although its poor hiding power in oil is reported in literature [113]. Degradation of azurite in *frescoes* seems related to pH and grain size [91, 114]. Azurite degrades to green compounds: malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) and paratacamite/atacamite ($\text{Cu}_2\text{Cl(OH)}_3$) are some examples [28, 64, 111, 112, 115–118]. Humidity and chloride ions from various sources cause the formation of black copper oxides (CuO) and green chlorides (nantokite CuCl, paratacamite/atacamite or botallackite $\text{Cu}_2\text{Cl(OH)}_3$ [103, 116, 118–121]). Azurite degrades to black tenorite CuO when exposed to heat in presence of alkali [20, 68, 91, 103, 113, 114, 121–123], while cold alkaline conditions might not affect it [111], or cause conversion to malachite [119], or the formation of tenorite via formation of copper hydroxide Cu(OH)_2 [35, 64, 114]. On the other hand, it is decomposed by acids, such as oxalic acid to form oxalates ($\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$, mooloite) [32, 55, 116]. It has been reported that the combination of oxalic acid and chlorides in wall paintings results in Cu-hydroxychlorides $\text{Cu}_2\text{Cl(OH)}_3$ and Ca-oxalates [59]; and that no Cu-oxalates were observed in azurite paint layers [58]. On the other hand, oxalates attributable to the biodegradation of an organic binder were found in both a gypsum preparation (weddelite/whewellite) and in the overlying azurite-containing paint layer [116]. Cu-carboxylates are rarely formed, as leadwhite, often mixed with azurite, is more reactive; moreover, as azurite is preferred in a tempera medium, carboxylic acids are less present [56]. In proteinaceous binder, other interactions are reported [51]. Verdigris $x\text{Cu(CH}_3\text{COO)}_2 \cdot y\text{Cu(OH)}_2 \cdot z\text{H}_2\text{O}$ might be formed when high relative humidity interacts with an azurite containing paint layer, degrading the oil binder [64]. Also, the yellowing of the binder/varnish can alter the blue shade to a green one in oil paintings [111]. Small particles are reported to have less colouring power and to be more sensitive to chemical interaction [35], and to dissolve in organic binding media [111]. In egg tempera, azurite is not affected by light, while thermal ageing, high relative humidity, and pollutants affect the paint film (oxidative processes) [112]. Also, the copper interacts with the proteinaceous moieties to form metalloproteins [112]. Azurite turns bluish-black when exposed to H_2S vapours [124], especially in *frescoes* [111], as covellite CuS is formed. The effect of laser irradiation on azurite is the formation of black CuO, which depends on the particle size and therefore on the temperature increase [112, 114, 125]. Selective biological activity is observed towards lead pigments [124].

Malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$, green)

Malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) is more stable than azurite ($2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) and verdigris ($x\text{Cu(CH}_3\text{COO)}_2 \cdot y\text{Cu(OH)}_2 \cdot z\text{H}_2\text{O}$), therefore showing less or slower reactivity towards many factors [119, 123]. It is known to be permanent in all binding media, light-fast and alkali proof. Its deeper colour is obtained by coarse grinding, and as a consequence of having relatively low refractive index, it shows better performances in tempera than in oil [50, 126]. Due to its chemical composition, malachite is subject to interactions with acids, bases, humidity, temperature and circulating ions. In presence of humidity, malachite stains can be observed, which are actually caused by proteinaceous binders degradation [64]. Moreover, ions such as Cl^- present in the mortar, sand or in the bricks, can react with the basic carbonate to form copper hydroxychlorides ($\text{Cu}_2\text{Cl(OH)}_3$) atacamite, clinoatacamite, paratacamite botallackite) [119, 121, 123, 126–128] and the copper chloride nantokite [103]. Sulphate ions are also likely to be present in wall paintings, especially from the degradation of calcite to gypsum, from gypsum preparation layers [53], or from SO_2/SO_3 pollution.

Copper basic sulphates ($\text{CuSO}_4 \cdot y\text{Cu(OH)}_2 \cdot z\text{H}_2\text{O}$: brochantite, langite, posnjakite, antlerite) are formed according to pH, humidity and temperature [119, 127, 129]. Copper chlorides and sulphates can further react to form other salts [127]. In tempera medium, it seems that the carbonate function is affected, more than in fat media, and more when no varnish is present to protect the paint layer from ageing [122]. Malachite particles in the form of spherulites were identified in brownish tempera layers, the discolouration being caused by the pigment-binder reaction [130]. In oil or oil/resin medium, it can turn into copper resinates [126] and other organometallic compounds [131, 132]. Copper carboxylates, originating from the binding media interacting with the pigment's cation, were observed for both tempera and oil binders [55, 133, 134]. Acidic conditions are commonly found in, and surrounding, polychrome objects, as a result of biological activity on the object [53] or of degradation of the organic binders (e.g. oxalic acid [129, 135]). Diluted acids decompose malachite (for example acetic, hydrochloric, nitric acid [126]), causing the release of Cu^{2+} ions, and the formation of the most stable phase according to pH and other present ions. The release of acetic and formic acid by the organic building materials of the display cases has been ascertained [136–138]. The copper oxalate mooloite was studied [32] and identified in various works of art [53, 135]. Bluish Cu acetates, corresponding to the well-known pigment verdigris, were identified on pure pigment powders exposed to acetic acid atmospheres [109]. H_2S vapours cause darkening by formation of the

bluish sulphide covellite, which is formed on the pure malachite pigment [126, 139], although in paint layers this has not yet been identified [124, 126]. On the other hand, it seems that Cu act as a biocide towards microorganisms that produce sulphuric acid, leading to a selective H₂S attack on non-copper pigments [124]. In *fresco* wall paintings, malachite can discolour due to the alkaline pH of the lime binders, especially when the particle size is small. The exposure to high temperature (fires) can lead to the formation of black copper oxides [1, 91, 103, 121, 139, 140], especially in *frescoes* due to alkaline conditions [126]. On exposure to laser light, pure malachite darkens [139], as a consequence of reduction of Cu²⁺ to form dark cuprite Cu₂O and black tenorite CuO [141, 142]. The same reactions take place when heating malachite above ca. 360 °C [125].

Verdigris (copper acetates: $x\text{Cu}(\text{CH}_3\text{COO})_2 \cdot y\text{Cu}(\text{OH})_2 \cdot z\text{H}_2\text{O}$, bluish green)

Verdigris is currently used to indicate a variety of blue-green compounds resulting from the exposure of copper to various acidic media (vinegar, for example) [1, 143]. The instability of verdigris is well known [50]. Improved performances seem related to oil/oil-resin rich paint layers, or to the selection of the neutral respect to the basic form (less reactive towards the acidity of the oil), or by adding yellow glazes on top of it [1, 144]. Verdigris is less stable than malachite and azurite to salt solutions, forming Cu²⁺ salts when the appropriate anions are present, such as nitrates, sulphates, chlorides [119, 123]. It promotes oil curing and it retards its oxidation [20]. Verdigris (neutral and basic), as well as the copper carbonate pigments azurite and malachite, shows the tendency to react with the oil binding media to form copper soaps [35, 67, 145], to brown and darken, as Cu⁺ is formed by ambient light absorption (photoreduction), and oxygen promotes the formation of brown peroxide species [146]. Cu-salts of organic acidic compounds are formed in verdigris-containing paint layers (or at the interface with the varnish), as fatty and resin acids can extract copper ions from the verdigris pigment [133, 147]. It seems important to mention that such reactions are equilibria, and therefore the addition of overpaint, or the removal of paint or varnish layers during restoration, might affect the chemical structure of the aged layer [133]. Copper acetates and resinates catalyse the oxidation process of oil films and influences the curing of the oil [133, 134, 147, 148]. In tempera, verdigris seems less prone to discolouration, but still reactions of Cu-extraction can take place [133, 146]. Copper acetates are very soluble in acidic conditions, and copper oxalates are formed in presence of oxalic acid from various sources [32]. In alkaline conditions, blue copper hydroxides are formed [20].

When exposed to H₂S, the pure pigment turns dark, as covellite is formed; however, this compound has not been identified yet in paint layers [20, 124]. Verdigris should not be mixed with orpiment or leadwhite, as darkening occurs [50]. Verdigris is not sensitive to lasers [141, 142, 149, 150], but it darkens during particle induced X-ray emission (PIXE) analysis [151]. It is involved in cellulosic materials degradation, especially for critic conditions of illumination and SO₂ concentrations [20].

Copper resinate (copper salts of abietic acid, green)

Copper resinate was used as a glaze, prepared by mixing Cu-acetates (verdigris) with oil and/or resins. In this process, some of the acetates remain unreacted [147]. When mixed with oil, the coordination of the copper ion changes [147, 151]. Copper carboxylates are formed from the oil fraction of the binder, while metalloproteins may appear if egg tempera was used [147]. It darkens with light exposure [98, 132] and in alkaline conditions [132]. Also, being an artificial pigment, its production process might affect its stability, if reactive moieties are not carefully removed [98]. The lipidic fraction of the paint layer undergoes photo-oxidation, with Cu acting as a catalyst: local molecular arrangement changes are likely to be involved in colour changes [20, 147]. Upon prolonged exposure to X-rays, Cu²⁺ is reduced to Cu⁺ [151].

Egyptian blue ($\text{CaCuSi}_4\text{O}_{10}$)

The artificial pigment Egyptian blue (a silica-rich glass, whose colour is related to the presence of the mineral cuprorivaite, CaCuSi₄O₁₀ [152, 153]) is a very stable pigment (to acids, alkali, light) [28]. It is related to Egyptian green, whose colour is due to the presence of Cu-doped (max 2%) parawollastonite (CaSiO₃), which does not show evident degradation issues (it transforms into the polymorph pseudowollastonite above 1150 °C) [154]. Egyptian blue requires coarse grinding to maintain its colour, showing poor hiding power [155]. Some discolouration can anyway be observed on Egyptian blue, towards greenish or black compounds. It is reported to degrade to a green coloured material as Cu²⁺ ions are leached and react with Cl⁻ ions from the glass itself or from circulating solutions to form carbonates and chlorides [156–158]. Degraded Egyptian blue was found to contain chlorides (atacamite and eriochalcite CuCl₂·2H₂O) [158]. Moreover, the yellowing/darkening of the organic materials (varnishes, gums) can alter the appearance of this blue pigment, and pigment-binder interactions could promote selective darkening, thanks to the release of copper ions from the pigment itself, possibly in relation to pH, impurities and gum type [155]. No evidence of black tenorite CuO formation was found [155, 159].

Copper chlorides (atacamite, paratacamite, clinoatacamite, botallackite: $\text{Cu}_2\text{Cl}(\text{OH})_3$, green)

The polymorphs of copper hydroxychlorides ($\text{Cu}_2\text{Cl}(\text{OH})_3$) pose relevant nomenclature issues, especially as regards paratacamite which is often used as a synonym for clinoatacamite, even though the two minerals have different formulas ($(\text{Cu},\text{M})_2\text{Cl}(\text{OH})_3$) and $\text{Cu}_2\text{Cl}(\text{OH})_3$, respectively, where $\text{M} = \text{Zn}, \text{Ni}$) [1, 160]. Chlorides of Cu were identified as pigments in objects from different cultures [1, 118, 161, 162], and recently atacamite was found in colonial art [163], in China [164] and in Alhambra's plasterwork [59]. As a pigment, it can be natural or synthetic, and the particles' morphology and composition can clarify its origin [162, 164]. It is expected to form as a degradation product of Cu containing pigments, or artefacts such as bronzes, in presence of humidity and chloride anions [115, 119, 121, 158, 160, 165, 166]. It is however not stable in acidic conditions (oxalic acid, for example), which promotes the formation of mooloite ($\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$) [127]. Also, among the polymorphs, different stabilities are observed, botallackite being the first formed and more unstable, while paratacamite seems the favoured species at ambient temperature [167]. The polymorph paratacamite has so far been identified as degradation product on other Cu-containing pigments [64, 117, 119, 123, 129]. However, an interesting example is reported in literature: after the 1966 flood in Florence, green paratacamite was formed on azurite-containing wall paintings [115]. To treat sulphated walls, ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) and barium hydroxide ($\text{Ba}(\text{OH})_2$) were used. The green paratacamite alterations turned blue after the treatment, but not permanently. In fact, in the alkaline conditions given by the treatment, paratacamite is dissolved by the ammonium carbonate, and blue $\text{Cu}(\text{OH})_2$ formed. This hydroxide is not stable and it degrades either to black CuO or to hydroxychlorides. This latter reaction is more probable due to the continuous ingress of Cl^- ions via capillary rise in walls, thus generating more green products, making this treatment not suitable in presence of degraded azurite [115].

Copper sulphates (brochantite, antlerite, langite, posnjakite: $\text{CuSO}_4 \cdot y\text{Cu}(\text{OH})_2 \cdot z\text{H}_2\text{O}$, green)

Green copper sulphates are commonly found as degradation products on copper artefacts exposed to polluted environments [105]. Brochantite was identified as a pigment as well [1], but it can transform into the more stable polymorphs, antlerite, langite or posnjakite, according to the given conditions of relative humidity, inorganic pollutants (SO_x) and biological activity (affecting the pH and the type of acids) [127, 129, 168]. Posnjakite was also identified as a pigment [162, 169]. Brochantite, as well as

posnjakite and antlerite are also intermediate reaction products between copper carbonates and copper oxalates, and are therefore sensitive to oxalic acid [127].

Arsenic (Z = 33)

Geologically, orpiment (As_2S_3) and realgar (As_4S_4) occur together, and are often associated with antimonates and other sulphides [1, 30]. Orpiment and realgar were highly appreciated especially in Egypt and China for their rich yellow and red–orange shades [1, 170–174], even though the pigments were considered “unpleasant” by many artists, and not recommended to use in combination with copper and lead based pigments, such as verdigris and leadwhite [1, 30, 170]. Orpiment and realgar exist as minerals, as well as synthetic pigments [175], and of the two arsenic sulphide pigments, the first one is the most stable. Realgar, being unstable, was less often reported in works of art [1, 176–179]. It has a polymorphic photodegradation product, pararealgar As_4S_4 . Permanence of arsenic sulphide pigments is problematic, especially on exposure to the green region of the visible spectrum [174, 180]. Moreover, smaller particles are more readily degraded [174]. The sensitivity to green light has to be taken into account when lasers need to be used, such as during Raman spectroscopic analysis [177, 181, 182]. Arsenates (As^{5+}) are formed from orpiment, realgar and emerald green degradation: these ions are water soluble and migrate throughout the whole painting, accumulating at interfaces between layers, around Fe/Mn rich particles, and according to the local pH conditions in the paint layer. Due to this water-based transport, appropriate cleaning solvents must be selected, and relative humidity controlled [180, 183]. It seems that polysaccharidic media, or egg yolk, negatively affect the stability of the arsenic sulphide pigments [184].

It needs to be pointed out that pararealgar was recognized as a mineral in 1980 [171], and that only recently the mechanisms of arsenic sulphides degradation was investigated [174, 183]. Care needs to be taken when considering published data, according to the year of publication and used techniques (compare for example [171] with [174]).

Orpiment (As_2S_3 , yellow)

Permanence of orpiment to light was known to be poor, although some intact paint layers could be found on some illuminated manuscripts [176, 178, 179]. Coarser grain size seem to retard the colour change [30]. In water, upon heating, and in oxidizing conditions (ozone, NO_x , for example) it decomposes to arsenic trioxide (As_2O_3), and hydrogen sulphide (H_2S) is formed as well in presence of humidity [9, 176]. Relative humidity alone seems to have no effect, while degradation is observed when

both humidity and light are present [64]. Light exposure causes discolouration [30, 128, 182, 185, 186]. Orpiment darkens upon heating, it burns in air producing white arsenolite (As_2O_3) and volatile SO_2 , and it decomposes in water (the artificial product having smaller particles, dissolves faster). It is soluble in many inorganic acids, and in alkaline conditions as well, which make the pigment unsuitable for use on wet plaster [123, 176]. It is reported to be unstable in oil [170]. When mixed with lead and copper pigments, darkening occurs, for example the case of leadwhite is reported in literature [30, 50, 176].

Realgar and pararealgar (As_4S_6 , reddish orange)

Realgar, exposed to light, degrades [30]. However, the formed yellow compound is not orpiment, as believed until 1980, but pararealgar [171, 187]. Exposed to (green) light, both high and low temperature realgar transform into brittle, bright yellow pararealgar [106, 177, 181], and finally to arsenic trioxide (As_2O_3) [106, 180, 188]. The phenomenon is complex and involves intermediate phases such as χ -realgar. Pararealgar is also to be considered an equilibrium phase [175, 177, 189]. Heating causes darkening of the colour of realgar, χ -realgar, as well as of pararealgar, which is not permanent: in fact the high temperature polymorph converts to the low temperature realgar with time [189]. As orpiment, it burns in air and shows similar solubility [176]. The role of the binder on realgar's stability is not completely understood, yet it could protect the pigment from discolouration [177]. Seen that the photodegradation of realgar yields a yellow material, which was long thought to be orpiment, but was finally identified as pararealgar [171], one might question the identification of orpiment in museum objects [177], as well as consider the possibility of pararealgar as a pigment [106, 173, 178, 190–192].

Mercury (Z = 80)

Vermillion (HgS , red)

The deep red coloured cinnabar (HgS), as well as its synthetic counterpart vermilion (HgS), produced either by wet or dry processes [193, 194], were extensively used [1]. Roman sources [195], however, seemed to use the term *minium* to identify this material, giving room to misinterpretations and nomenclature issues [1]. It was already known to Romans [195, 196] that mercury sulphide darkens when exposed to light, although not systematically [1, 193, 194, 197–199]. Moreover, HgS was not recommended for use in *fresco*, as humidity and pH affect its stability [103, 123, 200], but still it was used on wall paintings [73, 193, 201–203]. Paint layers of pure vermilion are very vulnerable [199], while no darkening is observed when it is mixed with leadwhite [19, 20, 193, 204]. An increased resistance to laser radiation is also observed

for other mixtures, such as vermilion with chrome yellow, madder, Prussian blue, and bone black, although the single pigments' behaviour is hardly predictable [19]. Red lead, often mixed with vermilion to improve the curing of the oil binder, seems to have a protective effect on HgS [20, 199]. A series of reactions of vermilion with other pigments, different binders and substrates are reported in literature [65, 198, 205]. The presence of a varnish layer, and of organic binders, moreover, seems to protect the paint layer, by absorbing the incident light (more effectively when the varnish is thick and/or yellowed, and with different efficiency according to the composition, i.e. UV light is strongly absorbed) and by physically protecting the pigment grains from contact with chlorine-containing materials (disinfectants, dirt, etc.) [199, 206]. Sulphation of the red paint layers in Pompeian wall paintings was observed, and seems to be connected with the Cl^- induced degradation of vermilion [106, 202]. The blackening of vermilion was often attributed to the formation of a black compound, supposedly metacinnabar (β - HgS) [194], although no positive identification could be obtained [198]. Binder type and pigment/binder ratio affect the pigment's stability, and glazes seem to have a role in preserving the red hue of vermilion, by filtering some of the incident light and protecting the pigment from external sources of chlorine [199]. The same metacinnabar is hypothesized in wall paintings [121, 139, 202], but only identified on laser irradiated vermilion [70, 142]. Pure vermilion is sensitive to lasers of various wavelength and irradiation, so that the original structure is lost [141, 142, 206]. Black β - HgS was identified by X-ray diffraction (XRD) on IR-laser damaged red α - HgS [70], and by X-ray photoelectron spectroscopy (XPS) [141]. Dark Hg_2S was detected as well, by XPS by [150]. XRD and XPS studies suggest a photoreduction of HgS to $\text{Hg}^0/\text{Hg}_2^{2+}$, instead of polymorph transformation [150]. Finally, the photodegradation of vermilion was explained in terms of formation of metallic mercury and HgCl_2 , due to the halogen impurities present in the pigment, identified thanks to secondary ion mass spectrometry (SIMS) analysis [207], and to X-ray spectroscopic analysis [208]. The role of Cl^- ions, present as an impurity in the pigment, coming from marine aerosol, from the used binder or from pollution, in the degradation of vermilion has been ascertained thanks to the identification of chlorine species [197, 199, 202, 203, 207–209]. Calomel (HgCl_2) was identified by portable and micro-Raman spectroscopy, while HgCl_2 and metacinnabar were not [33, 59, 73, 199]. The photosensitivity of vermilion depends on one hand on the presence of halogen impurities [199, 202, 207], and on the other on the particles' size and relative humidity [64]. The cause of the discolouration is, however, still under debate (elemental mercury or dark

Hg–S–Cl species, as well as grey mercury chlorides) [33, 73, 199, 207]. In tempera, vermilion is only slightly sensitive to 248 nm laser pulses, while in oil medium it shows the lowest discolouration threshold for that laser wavelength compared to a selection of pigments [19, 193, 199, 210]. It is also reported that in oil medium the darkening is worse than in watercolour [194]. In this latter case, vermilion is reported to be sensitive to light, with oxygen and humidity accelerating the darkening [66]. No mercury oxalates were ever identified on vermilion paint layers [56].

Lead (Z = 82)

Lead pigments are not suitable for use in *fresco*, but they were still used due to their good hiding properties and to the low prices compared to other pigments [5, 123, 200, 211–213]. The degradation processes of the various Pb pigments yield a range of compounds which cause discolouration, strongly affecting the readability of the polychromy [200]. Lead pigments on ceramic artefacts are sensitive to sulphur containing pollutants, to acidic solutions (rain; CO₂; microbial activity), to light and air: anglesite PbSO₄, cerussite PbCO₃, hydrocerussite 2PbCO₃·Pb(OH)₂ and lead sulphide PbS are formed [166]. Anglesite, attributed to lead pigment degradation was identified on wall paintings as well [214]. To laser irradiation, reduction of the lead compounds (leadwhite, massicot, red lead) occurs on the surface, so that the dark colour is attributed to formation of metallic lead, or Pb₂O [150]. The subsequent oxidation of lead explains the reversibility of such a colour change [150]. The temperature increase related to the laser irradiation causes the formation of massicot on both minium and leadwhite [150]. Care needs to be taken when a laser source is used for analytical purposes, such as during Raman spectroscopic investigations, as the lead pigments and their degradation products, such as PbO₂ and PbS, might be altered, affecting the interpretation of the degraded areas [215, 216]. All lead pigments turned black after exposure to H₂S vapours (formation of galena, PbS), with increasing reactivity for basic moieties, such as Pb(OH)₂ units in leadwhite [124]. It is reported that biological colonization on wall paintings can selectively affect lead (II) compounds, causing brown discolourations identified as PbO₂ or PbS [211, 217], while copper pigments act as biocides [124, 212]. Lead dioxide formation is favoured in humid alkaline conditions, such as in *frescoes*, when peroxides are produced, either by microorganisms or by photo-oxidation of organic materials [213]. When exposed to salt solutions, and light, the most stable phase for all the lead pigments is cerussite [123, 200, 218]. In oil, lead compounds were not only used as pigments, but as siccatives as well [219, 220]. Moreover,

lead soaps are formed in, or on the surface of, oil paint layers containing lead based pigments (leadwhite, lead tin yellow type I, litharge, red lead) and are investigated as they affect the appearance of paintings [54, 55, 107, 145, 219–228]. Lead oxalates were observed on leadwhite treated with oxalic acid [32], and on real samples containing red lead and lead tin yellow [56]. Plumbonacrite 3[2PbCO₃·Pb(OH)₂]·PbO was detected as well [56].

Leadwhite (2PbCO₃·Pb(OH)₂)

The term “leadwhite” refers to a variety of white lead based materials, of which the most common, and most important from the artistic point of view is the basic lead carbonate corresponding to the mineral hydrocerussite (2PbCO₃·Pb(OH)₂) [1, 229], possibly including cerussite as well, according to the fabrication process [1, 20, 229]. Considering it is a carbonate, it is relatively stable, although soluble in acids [20, 98, 229]. Also, it shows catalytic effects [230]. Upon heating, massicot (orthorhombic PbO) is formed, then litharge (tetragonal PbO) and finally red lead (Pb₃O₄) [229]. It was used in every medium. Black discolouration is observed on frescoes and watercolours [20], and it is reported for manuscripts as well [60, 231]. The blackening is attributed to the formation of either PbO₂, as a result of exposure to oxidizing agents or from microbiological activity, or PbS [9, 20, 98, 200, 211–213, 232]. The role of S-containing pigments on the blackening of leadwhite is not fully understood [191, 229], while atmospheric and biological sources of H₂S strongly affect watercolours [20, 191, 231] and manuscripts [60, 190, 191, 204]. If PbS is formed, a reconversion treatment (oxidation) can be applied to restore the white shades of degraded polichromy. However, the formed lead sulphate (PbSO₄) is not sufficiently stable to make the treatment recommended [139, 212]. Humidity seems to be involved in many degradation processes, especially in synergy with atmospheric pollutants such as SO₂ and NO_x [9, 64, 166]. The presence of sulphuric pollutants is responsible for the formation of lead sulphide, lead sulphates, and cerussite/hydrocerussite [124, 166]. The sensitivity of leadwhite to laser light was studied extensively, especially with respect to laser cleaning and laser based analysis of works of art, but the alteration process is not fully understood, the binding medium probably influencing the results [70, 142, 150, 210, 215, 233, 234]. Analytical evidence of formation of metallic lead and lead (II) oxides upon IR laser irradiation is provided in literature [70, 234]. A visible laser (632 nm) caused the appearance of a massicot-like alterations on leadwhite, possibly via a plattnerite (PbO₂) intermediate, which is related to impurities in the leadwhite [72]. Low fluence UV-laser does not affect paint layers prepared with different binders [235]. Moreover,

the exposure of the PbO degradation to environmental conditions is likely to yield a carbonate-hydroxide lead salt, making the degradation reversible to some extent, especially in absence of a binder [19, 142, 234]. The influence of ion beam based analysis on polychrome objects can negatively affect leadwhite paint layers, as hydrocerussite is sensitive to PIXE analysis [151]. On wall paintings, the combined presence of humidity and salts can cause the formation of degradation products, sometimes coloured as in the case of $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$ and PbO polymorphs, with cerussite being the most stable of them all [123, 218]. Leadwhite tempera and oil layers show the formation of lead soaps, which negatively affect the appearance of the paintings [55, 67, 226]. Leadwhite tempera applied on *fresco* paintings yields PbO_2 , as the reaction takes place in alkaline environment [213]. Also, differences in naturally and artificially aged samples are observed, the latter being less degraded [230]. Lead oxalates were observed on leadwhite treated with oxalic acid [32], and on real samples [56]; lead acetate was detected upon exposure to acetic acid [109]. Plumbonacrite ($3[2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2] \cdot \text{PbO}$) was detected as well [56].

Litharge (PbO, orange)

In antique sources, the term litharge denotes a variety of compounds derived from lead oxidation, and other compounds. It is now recognized as the low temperature polymorph of PbO, which is tetragonal [1]. As a pigment, it was identified on manuscripts and mural paintings [1]. It is less stable than massicot to water and to saline solutions commonly found in wall paintings [218]. As a pigment, litharge is stable to infrared (1064 nm) and red lasers (632, 647 nm) irradiation for Raman spectroscopic studies [215, 233]. Using a 632 nm laser with a power above 9 mW (calculated fluence of approximately 45 kW/cm^2) degradation is recorded [215]. For shorter wavelengths, and laser fluence at the sample above 2 kW/cm^2 , litharge degrades to massicot [215]. In oil and tempera binder, lead carboxylates are observed, showing stronger intensities compared to those formed from lead white [55]. This increased reactivity was probably well known to artists and artisans, as PbO was often used as a siccativ for binders and varnishes [1]. Litharge was as well used for the preparation of other pigments [236]. It degrades to cerussite and hydrocerussite, as well as to lead sulphate and phosphate, in archaeological sites attributed to the production of painting materials in Thera, Greece [236].

Massicot (PbO, yellow)

Also in this case, as for litharge, nomenclature is complex and confusion may arise. Massicot corresponds to orthorhombic PbO, the high temperature polymorph of

this compound [1]. It is reported as a pigment in Egyptian artefacts, mural paintings and manuscripts [1]. On wall paintings, the presence of water and of bicarbonate ions from atmospheric CO_2 dissolution causes the formation of hydrocerussite and cerussite, the latter being the most stable compound of the series, even when intermediate salts are formed according to the present anions in the saline solutions [123, 218]. As for other lead containing paint layers, humidity causes first a darkening of the colour, and finally the formation of leadwhite [64]. Upon exposure to H_2S , black galena (PbS) is formed in a thin superficial layer [124]. Massicot is stable to laser irradiation, except to 10 mW of 514 nm laser, where a whitish degradation is observed [215]. The effect of infrared laser irradiation was investigated as well and it was found to cause reduction of the pigments, and discolouration due to the formation of metallic lead. This process is very intense for massicot, as the formed metallic particles are hardly subjected to re-oxidation, due to their bigger size [150].

Red lead (Pb_3O_4)

Red lead, or minium, has a long history of use in worldwide artistic and artisanal practices, although nomenclature issues are evident [1, 237, 238]. Its synthesis and relation with the other lead oxides is well described in literature [238]. As a pigment, it is not stable in *fresco*, or in watercolour. It was anyway used, for its optical properties and cheap price, compared to other red pigments [1, 120]. It is reportedly blackened on manuscripts and in glue tempera paintings exposed to light and humidity [1, 64]. On the other hand, it is reported that medium-rich proteinaceous red lead paints are stable to light, the binder protecting the pigment [239]. Moreover, the pigmented layer has different properties than an unpigmented one [51]. It is soluble in diluted acids (nitric, chloridric, oxalic, acetic), with formation of the corresponding salts, and when heated it transforms to litharge [1, 240]. It is sensitive to sulphur containing compounds, as H_2S and SO_2 of atmospheric or biological origin, and pigments such as arsenic sulphides (As_xS_y), vermilion (HgS) and ultramarine ($\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{S}_n$), especially in manuscripts, wall paintings, and in case the pigment is not mixed with a binder, which cause the formation of dark grey PbS [1, 60, 93, 124, 238, 241] and of whitish PbSO_4 [59, 68, 233, 242]. This was known to artists and artisans, as demonstrated by the presence of a blank space between yellow orpiment and red lead in a 12th century illuminated manuscript, although mixtures of the two pigments do not behave consistently. The reaction between red lead and orpiment produced galena, which could further degrade into sulphates, and lead arsenate species [241]. Mimetite $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ was as well identified as a reaction product

of minium and orpiment [186]. Moreover, it seems that minium promotes the blackening of leadwhite, when the pigments are mixed [204]. Some cases of red lead lightening are reported as well, and are related to the formation of lead sulphates and/or carbonates, according to the atmospheric pollutants and to the initial amount of PbO in red lead [68, 93, 200, 237, 238], via the formation of plumbonacrite [228].

The black discolouration of red lead due to light exposure was initially attributed to the formation of black PbO₂, but this compound is not stable to light [1], and it was rarely positively identified [93, 120, 238], while mixed oxides are also hypothesized [59]. PbO₂ could be a metabolite of microorganisms such as fungi [217, 239]. The parameters responsible for the blackening of minium are identified as light [5, 240, 243], including laser light (514 and 488 nm, [215]), the pigment's composition, and climate. These parameters all contribute to yield a grey discolouration at first, and finally a chocolate brown one [240]. Red lead semiconductor properties are responsible for the reduction of Pb(IV) to Pb(II), and the formation of PbO; the presence of bicarbonate ions (HCO₃⁻) promotes then the formation of hydrocerussite and/or cerussite [123, 218, 244]. The PbO formed by laser irradiation can be re-oxidized to minium [142]. A role of Cl⁻ ions is also hypothesized [93, 245]. The formation mechanism of black discolouration products [plattnerite (PbO₂) and galena (PbS)] was recently investigated: no plattnerite could be detected in artificial ageing tests, while the natural ageing of *fresco* red lead samples yielded calcite CaCO₃, minium Pb₃O₄, plattnerite PbO₂, anglesite PbSO₄ and gypsum CaSO₄·2H₂O, with the minium grains being gradually converted to alteration products (plattnerite and anglesite) via a sulphation step followed by solvolytic disproportionation [237, 242]. Plattnerite might be formed if acidic pollutants attack the paint layer [242]; or when biological colonization is present [238]. Red lead is readily affected by organic acids (including the oil binder), which causes the final appearance of lead carbonate, via lead acetate Pb(C₂H₃O₂)₂ [109] and lead hydroxide Pb(OH)₂ [55], and/or lead soaps [67].

Lead tin yellow (type I: Pb₂SnO₄; type II: PbSn_{1-x}Si_xO₃)

Two types of yellow pigments based on lead and tin are available, type I which is an oxide (Pb₂SnO₄), and type II which is a stannate silicate of lead (PbSn_{1-x}Si_xO₃). On their nomenclature, chronology, and occurrences, more can be found in literature [1, 20, 246], and references therein. As pigments, they show good hiding power and siccative properties when used in oil [246]. Other than for use as pigments in paintings, lead and tin-based coloured opacifiers were used in glass making [1, 20, 246]. Both pigments are stable to alkali, but sensitive to H₂S

and sulphides, which causes blackening (PbS) [246]. Whereas other lead containing pigment show fire damage, lead tin yellow type I is detected unaltered [245], but heating above 900 °C causes decomposition of the material [20, 246]. They are lightfast, opposite to the other Pb based yellow pigment, massicot (PbO), and stable in oil medium [20, 246]. Relative humidity has no negative effect on either pigment [64]. On the other hand, acidic components interact with the materials, including carboxylic acids from the ageing oil (lead soaps [56, 225, 247]), or volatile organic compounds, such as acetic acid, of relevance in air quality evaluation in museum environments (lead acetate Pb(C₂H₃O₂)₂ [109]).

Conclusions

The general understanding of the on-going potentially harmful processes regarding inorganic mediaeval pigments is almost completed, and benefitted from the development of new analytical techniques. This work, based on chemical and archaeometrical literature, summarizes both evidences of pigments discolouration and degradation in works of art, as well as investigations based on mock-ups and simulations. Also, results from a variety of analytical techniques are here considered, as the complexity of the topic requires. In fact, tracking and understanding the reactions causing discolouration of the studied pigments requires a different approach according to the problem: salt dissolution and formation (Ca, Cu and Pb-based pigments); reduction or oxidation reactions (Fe, Cu, Hg, Pb-containing pigments); ions leaching (ultramarine, smalt; Ca, Cu, Pb-pigments); polymorphism and structural modifications of the materials (Cu, As, Hg and Pb-pigments). In each case, an adequate selection of analytical and imaging techniques should be made. Moreover, the role of light (illumination, or laser systems) needs to be taken into account, especially for photosensitive pigments (As and Hg-containing). Finally, humidity, pollutants and contaminants (H₂S, SO₂/SO₃, NO_x; Cl-compounds) provide reactive moieties.

The collected information regarding the stability of mediaeval inorganic pigments shows how complex the conservation of polychrome objects can be. First, the understanding of the pigments' stability to specific factors is required. Even though pigments are not often present without binder in works of art, it is important to know their reactivity. Then, the study of pigment-binder interactions, and how they affect the single components and the paint layer itself needs to be considered. Finally, the implementation of air quality control systems and climatic monitoring should take into account the different sensitivities of each and every material in museums and exhibitions, in storage or on display, in order to ensure its preservation for the future generations.

Abbreviations

MEMORI: Measurement, Effect Assessment and Mitigation of Pollutant Impact on Movable Cultural Assets. Innovative Research for Market Transfer; UV: ultraviolet; IR: infrared; μ : micro; FTIR: Fourier transform infrared spectroscopy; ATR- μ -FTIR: attenuated total reflection micro Fourier transform infrared spectroscopy; SR: synchrotron radiation; μ -SR-FTIR: micro synchrotron radiation Fourier transform infrared spectroscopy; XRD: X-ray diffraction; μ -SR-XRD: micro synchrotron radiation X-ray diffraction; Nd:YAG laser: neodymium doped yttrium aluminium garnet; XAS: X-ray absorption spectroscopy; PIXE: particle induced X-ray emission; XPS: X-ray photoelectron spectroscopy; SIMS: secondary ions mass spectroscopy; RH: relative humidity.

Authors' contributions

AC performed the literature review, and compiled the text of the manuscript. LM and PV supervised the work, provided feedback on the manuscript and general guidelines for the redaction of the review. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

Availability of data and materials

This review is based on published literature, therefore no datasets/databases exist.

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