

Review

# Mineral Pigments in Archaeology: Their Analysis and the Range of Available Materials

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**Abstract:** Naturally occurring minerals or their synthetic analogues have been important as pigments used in artistic and cosmetic contexts in global antiquity. The analysis and identification of mineral pigments, though routine to the petrologist or mineralogist, also requires specialist knowledge of the archaeological contexts and available technologies and trade. This paper attempts to present an analytical approach to the study of mineral pigments in archaeology and also introduces the range of mineral pigments encountered in works of art and painted objects on archaeological sites and in museums. It attempts to cover the range of mineral and synthetic inorganic pigments used in global cultures from the early Medieval period.

**Keywords:** pigments; artists' pigments; materiality; minerals; archaeology; paint

## 1. Introduction

As long as people have been making marks, they have been using pigments. As is always the case in archaeology and history, our attention and knowledge is restricted to preserved evidence, but it can be assumed that pigments were made into paints to produce temporary and permanent marks on objects, the landscape and the human body throughout the Later Pleistocene and into the Holocene/Anthropocene. Earliest evidence of red ochre extraction extends back to 300 to 200 ka in Africa. A recent publication has demonstrated that modern humans were not the first species to use pigments and therefore create art; Hoffman et al. [1] have shown that cave paintings in the Iberian Peninsula can be dated to 64.8 ka and there is evidence of the manipulation of pigment materials for several millennia before this date.

The scientific analysis of artists' pigment is not a new field of research; indeed, it predates most modern science. The pioneer chemist Sir Humphrey Davy had studied the works of Classical authors Theophrastus [2], Vitruvius [3] and Pliny [4] and examined samples he had himself collected from a number of Mediterranean Classical sites including the 1st Century CE Nozze Aldobrandini painting, and paintings from Baths of Titus and the Baths of Livia in Rome and at Pompeii [5]. Using wet chemical methods, Davy accurately identified the pigment phases identified by the Classical authors in the pigments. At the time of writing, the study of pigments in painting from archaeological through historical periods has become a well-established field of research and an important aspect of forensic art historical investigation.

Within the study of materials in art, a pigment can be defined as the component of a paint that contributes colour. This is usually a dry, solid material that can retain its colour when ground to a fine powder (typically between 1 and 40  $\mu\text{m}$ ). To produce a paint, the pigment must be mixed with a binder or "medium" which is typically an organic compound such as gum Arabic, various plant-derived oils, wax and egg-yolk, amongst many others. Pigments can be combined with limewash to produce paintings in the fresco technique and (non-permanent) body paints could be a simple mixture of pigment and water.

Traditional, non-synthetic pigments are extracted from plants (for example the dyes indigo and madder and also charcoal and related materials), from animals (for example purple-coloured dyes extracted from molluscs, cochineal extracted from beetles as well as black and white pigments manufactured from bone and ivory) and from minerals encountered in the geological environment. Pigments can be synthesised by a range of chemical and physical processes, and indeed, one may speculate that the production of the first synthetic pigment dates, probably, to sometime in the later Pleistocene, when someone first discovered that a yellow ochre could be heated to produce a red ochre. Since the Bronze Age, synthetic pigment phases have been routinely produced with chemistries and structures analogous to naturally occurring minerals.

The focus of this paper will be the use and identification of mineral pigments and their inorganic synthetic analogues within archaeological contexts. I will attempt to review the most important applications of mineral pigments in art history globally from the Palaeolithic to the early Medieval period as well as some important uses of mineral pigments in modern hunter-gatherer societies. This is no small task as human innovation knows few boundaries with respect to materiality and innovation and new uses of minerals as pigments are regularly being discovered as the scientific analysis of painted objects becomes more widespread. As a consequence, this paper cannot be exhaustive, but its intent is to demonstrate the range of minerals used to create art and their relationships to culture, trade and geography. As I have attempted to take a global approach, dates will be recorded in thousands of years before present (ka) and the abbreviations BCE and CE will be used to denote Before Common Era (prior to year 0) and Common Era (year 0 to the present day).

## 2. A Cautionary Word on Terminology and Analysis

The vast majority of inorganic pigments are either naturally occurring minerals or synthetic phases which are chemically and structurally analogous to naturally occurring minerals (or indeed, can potentially be present in both natural and synthetic forms), and therefore a mineralogist has the ideal skill set to characterise the materials used in a painted artwork. However, herein lies a warning to the scientist engaged to identify pigments on painted surfaces. It is essential that the scientific analysis of works of art considers the context in which that work of art was created. If at all possible, mineralogists should collaborate with conservation scientists, archaeologists and forensic art historians so that data may be correctly and appropriately interpreted. The routine analytical techniques used for the analyses of mineral pigments and their synthetic analogues are polarised light microscopy (PLM), Raman microspectroscopy and X-ray Diffraction (XRD). Eastaugh et al. (2008), have produced a reference atlas of pigments observed using PLM and an experienced petrologist can provide identifications of pigment phases as well as pigment mixtures using this technique alone. Slides are most effectively produced as grainmounts, referred to as “dispersions”. Because of the very high refractive index (RI) of many pigment phases, the standard mounting medium should have an RI = 1.662. Otherwise, optical properties are the same as those used in routine petrological examination of thin sections, however particle size can be very fine (<5 µm) and access to an optical microscope with a 100× oil objective is essential. A benefit of pigment dispersion mounts is that the same slides can then be used for single grain analysis using Raman microspectroscopy. A large amount of literature is available on the identification of pigments using Raman spectroscopy, and comparative databases have been produced. The interested reader is referred to the work conducted at UCL under the direction of Robin Clark [6,7]. There have also been special issues of the Journal of Raman Spectroscopy devoted to the analysis of cultural heritage. XRD and other techniques in routine use for mineral analysis (i.e., transmission electron spectroscopy TEM, scanning electron microscopy with energy dispersive X-rays SEM/EDX, IR spectroscopy etc.) are becoming widely used for the identification of pigment phases, though analysts must be wary of vagaries of peak-fitting software as discussed below. Non-invasive techniques have huge advantages when it comes to the analysis of valuable works of art. Hand-held devices such as portable X-ray Fluorescence (pXRF) and portable Raman spectrometers have become the go-to devices for analysis of objects in situ. UV fluorescence and use of the Chelsea

filter [8] are also useful tools for distinguishing pigments on painted surfaces that cannot be sampled. It is always recommended that multiple techniques should be used to confirm analyses, and these should include PLM as this is the only technique that can distinguish pigments on the grounds of colour and habit and mixtures of pigments. For example, various forms of calcium carbonate (for example; chalk, oyster shell, avian eggshell and coral) can only be distinguished by microscopy.

Poor, incomplete or naïve scientific analyses are the bane of the forensic art historian. Some common pitfalls that the scientist embarking on a study of paintings should be aware of are outlined below. As with all black-box analytical techniques, analysts using such equipment must remember that these machines do not have a brain and that the data need to be interpreted with respect to the range of pigments available. First of all, it is important that a separate terminology should be used to distinguish naturally occurring minerals from synthetic phases occurring as pigments. A pertinent example is the red, mercury sulphide mineral cinnabar. This phase has been synthesised since antiquity and the synthetic equivalent is called vermilion. Both varieties have been used as artists' materials in many regions of the World and as valuable pigments they have been important trade commodities. The words "cinnabar" and "vermillion" therefore convey very different meanings in terms of availability, procurement, processing and therefore the value or prestige of these pigments within a human society. They represent different choices made by artists and patrons.

Similarly, XRD peak-fitting software might identify a yellow pigment as the mineral greenockite (CdS). It is highly unlikely that this naturally occurring mineral has ever been used intentionally as a pigment. The phase analysed is in fact the chemically and structurally analogous modern synthetic phase known as Cadmium Yellow, a pigment used widely since the mid 19th century. To report the occurrence of "greenockite" in an analysis of an artwork would not only be incorrect but could lead to the wrong conclusions and therefore spurious knowledge proliferating through subsequent literature.

It is also important to remember that traditionally, paints were made by people, often in dusty, dirty, non-sterile environments. Their composition is therefore not fixed. Various preparation methods would have been employed, including grinding and mixing. It is important to combine analytical chemical or spectroscopic techniques with PLM, to get an idea of the colour of the pigment phases used and whether pigment mixtures, fillers or impurities are present in the paint. For example, many green paints may be simple mixtures of a yellow and blue pigment rather than a single green-coloured phase. Alternatively, trace amounts of one paint might have contaminated another, but overall had minimal impact on the observed colour. Colour itself can be deceptive. A bright-red paint may be analysed as calcium carbonate, a material assumed to be white. The actual pigment is probably an organic dye such as carmine (cochineal) on a chalk substrate, composed of light elements not detected by conventional techniques. Or the substrate may be another form of calcium carbonate such as crushed mollusc shell, avian eggshell, coral, or even a synthetic precipitate. A "black-box" analytical technique used in isolation would not be able to distinguish these components. Organic pigments have also been widely used since the Neolithic, and probably earlier, and discussion of their origin can be found in the literature on dyes. Although beyond the scope of this current article, it should not be forgotten that many red, blue, yellow, green and purple pigments may contain at least one organic component, and specialists techniques (and analysts) such as gas chromatography mass spectrometry (GC-MS) are required for their identification.

The greatest hope of a scientist working for the first time on an archaeological artefact or a painting, is that they are going to find something novel and previously unknown. Although this does happen, it is a rare event. In reality, the analysis of, say, painted Egyptian mummy-cases is as routine as the analysis of granites, and the range of expected materials is similarly limited. Certain pigments were only available and in use during certain periods, and for most phases, this "first" and "last-appearance" is well documented. For example, in Dynastic-Period Egypt, the rock lapis lazuli was in frequent use in jewellery and other decorative stonework, and yet there is no evidence that it was used in this period in its pigment form (the colour dominated by the sulfur-bearing hauyne mineral lazurite—more commonly known as "ultramarine"). To discover an ultramarine-based paint on a mummy case might

therefore be seen as a major discovery. However, such a find is much more likely to be an analytical error or alternatively the artwork has been restored or it is a forgery. The technological knowledge required to extract the mineral lazurite from lapis lazuli is considerable and was not known to exist until the 6th Century AD. Such knowledge cannot exist in isolation in societies both ancient and modern, so a one-off, unexpected discovery is a rare event in reality. Take care with the interpretation of results, be very wary of over-interpretation and do not underestimate the knowledge of materials already present in the fields of archaeology and technical art history.

This article will now examine the range of minerals and mineral analogues used in archaeological and ethnographic contexts, in effect, in pre-mechanised, pre-industrial societies.

### 3. Earth Pigments

The earth pigments are ubiquitous in painting from most archaeological contexts. They may be broadly divided into iron-rich ochres, wads (manganese-rich ochres), umbers, green earths (terres vertes), white earths (chalks, kaolinite and diatomite), coals and other solid hydrocarbons and vivianite-rich blue earths. The earth pigments are not pure, single mineral pigments but share the property of being mixtures of possibly several chromophore minerals plus accessory phases including but not limited to, clays, carbonates and quartz. As deposits on the Earth's surface, they would have been both obvious and attractive sources of pigment, and it is this group of pigments that are of greatest importance in the production of prehistoric art.

#### 3.1. Ochres

Geologically, we can define ochres as earthy, metal oxide- or metal oxide hydroxide-rich deposits which form in the surface or near-surface environment. The most commonly encountered ochreous deposits are iron-rich, although copper and cobalt ochres have also been exploited for pigment use, and manganese ochres (wads) will be considered separately below. Naturally occurring ochres are by definition impure deposits containing a mixture of mineral components, commonly quartz, carbonate, clays and/or micas as well as metal sulphides. They are encountered as primary ochres, lying in close association with ore bodies or as secondary ochres subsequently concentrated in sediments and soils. Commonly these are soft and friable and therefore easily excavated and processed.

In the world of pigments and art history, the term "ochre" generally refers to iron oxide and oxide hydroxide rich powders with variable amounts of manganese oxides (Eastaugh et al. [9] and references therein). Red ochres are dominated by hematite and yellow ochres are typically dominated by goethite, though jarosite group mineral-rich yellow ochres are of local importance. The definition of ochres also includes ferrihydrite-rich ochre deposits formed as the result of natural acid rock drainage (NARD) and acid mine drainage (AMD) which tend to revert to goethite [10,11]. Such deposits are concentrated in streams and rivers and their locations would have been remarkable as well as colourful to pre-industrial eyes (Figure 1). The use of ferrihydrite as ochre pigments has been poorly documented, primarily as it readily converts to goethite over time, but it is extremely likely that NARD deposits would have been used to procure colour.

Yellow goethite ochres can be heated and are easily converted to red ochre of various shades when exposed to temperatures in excess of ~250 °C. Structurally disordered hematite has been encountered in the archaeological record [12]. Analyses of experimentally burnt ochre conducted by the author, Spike Bucklow, Onya McCausland and David Dobson (*pers comm*) using XRD, have shown that a high purity goethite ochre converted to well-crystallised hematite after 45 min burning in an open air, wood fire, disputing the claims that "disordered" hematite is evidence for primitive heat treatment [13]. As such, evidence of ochre burning in the archaeological record may be impossible to determine. David et al. [14] analysed ochres from the Egyptian site of Tell el-Amarna and found that yellow ochre pigments contained impurities of well-crystallised carbon, whereas red pigments were red ochre containing impurities of amorphous carbon. The interpretation of these results is that the red ochre was a burned version of the yellow. Controlled modification of colour through

heating ochres has become standard practice within the historical period paint manufacturing industry. The colour of natural “raw” ochres is related to their composition (relative proportions of hematite and goethite  $\pm$  manganese oxides; see Elias et al. [15]) and also particle size and the uniformity of particle size. The latter property has been shown to have a marked effect on the extensive range of colour exhibited by natural ochres collected from Clearwell Caves in the Forest of Dean, England [16,17].



**Figure 1.** Natural acid rock drainage precipitating ferrihydrite in the head waters of the River Fleet, on Hampstead Heath, London. The occurrence of these ochres are extremely noticeable features on the landscape. Photo. R. Siddall.

A major problem with red ochres is that they are extremely difficult to provenance, especially when highly processed. The presence of quartz or carbonate can be helpful in differentiating broad sedimentary environments, as can crystal habit (if preserved), colour (if not heat treated) and particle size (if not overly ground). A good field knowledge of the character and mineralogy of preserved ochre deposits in the vicinity of an archaeological site can be instrumental in securing provenance of local use [18]. However, ochre had status in societies and as a commodity it was traded over long distances [19]. White et al. [20], in an important piece of work at the Purijarra rock shelter in central Australia, was able to provenance ochres sourced regionally based on a cluster analysis of major minerals and trace elements, made on both ochres sourced at the site and known Aboriginal ochre pits across Australia. A similar study was made on a smaller scale by Eiselt et al. [21] from Hohokam and O’odham prehistoric sites in Arizona; ochre played a key role in the societies of the Gila River Valley, where it was used for body paint, rock art, other aspects of craft production and in mortuary contexts.

### 3.1.1. Red Ochre

The use of red, hematite-rich ( $\text{Fe}_2\text{O}_3$ ) ochres as pigments is global and they have been recorded in all works of art of all periods and traditions. As a pigment, it has been in continual use from the Pleistocene to the present day. The processing of geological ochres to transform them into ochre pigments is straightforward and involves a *chaîne opératoire* involving removal of larger impurities (including plant roots and other organic contaminants), grinding, sieving and/or levigation before adding to a medium to produce a paint. Ochre-derived pigments were and are also widely used as body decoration and sun protection, medical use, adhesives and as paints (slips) used to decorate ceramics as both pre- and post-firing treatments. Partly due to its preservation, evidence of intentional uses of ochre are associated with almost all excavations of both anatomically modern humans (*Homo sapiens*) globally and with Neanderthals in Europe. Arguably, in addition with stone suitable for tool making,

the procurement, preparation and application of ochres is arguably the earliest exploitation of Earth materials and the burning of ochres to modify their colour is the earliest form of pyrotechnology. In recent and modern hunter-gatherer societies such as the Kalahari Bushmen, Australian Aboriginals and the Peoples of the Pacific Northwest Coast and southwest USA, ochres and particularly red ochres have great significance in representing abstract concepts such as vitality, birth/rebirth and fertility, and there is reason to suggest that Palaeolithic societies would have imbued red ochres with the same powers. However, it should also be remembered that the colour red is bright and noticeable and deposits of red ochre would have been ubiquitous and obvious in a (pre-agrarian and pre-urban) landscape and such localities indeed may have been associated with supernatural properties [20]. Red ochre was the colour of the Palaeolithic and in all cases described below, hematite was the predominant chromophore in these pigments. To provide a comprehensive review of the global and temporal use of iron ochres in pre-Neolithic archaeology is well beyond the scope of this paper, nevertheless I will endeavour to cover some key Palaeolithic sites and discoveries.

Numerous early uses by humans from the Middle Stone Age (MSA) of Africa (280–50 ka) include evidence for ochre mining and processing in southern Africa [22]. Henshilwood et al. [23] excavated at the 100 ka Blombos Cave site in South Africa where clear evidence of red ochre processing and pigment preparation is in evidence. Raw ochre, grindstones, palettes and *Haliotis* sp. shells used for storage have been discovered.

Red Ochre was excavated in the Pleistocene (Middle Palaeolithic) age. These sites have been excavated in the Maastricht-Belvédère loess and gravel pit. Sediments here are associated with MIS 7, dating from 250 to 200 ka. These strata are relatively iron-poor, and ochres do not occur within this sedimentary sequence, but fifteen, very pure, red hematite “concentrations” with sharp margins with the enclosing sediments were found in association with flint tools and debitage. Roebroeks et al. [24] have interpreted these as drops of ochre paint, perhaps used on bodies or for some other unknown purpose. If this is the case, then this is the earliest use in Europe of ochres, with a date equivalent to earliest uses in Africa. In Eurasia, the Mousterian period (160–40 ka; Late Pleistocene) is predominantly associated with a few sites in the Near East showing a brief period of occupation. At Qafzeh Cave in Galilee, humans were buried in association with lumps of red ochre as well as *Glycymeris* sp. shells with red ochre stains on the concave surfaces. These shells were worn as body ornaments and could potentially also have been used as pigment containers. This deposit has been dated to 92 ka [25]. It is worth noting that mollusc shells have played a huge role in the history of pigments, being universally used for the storage of paints and pigments.

Other findings of use of ochre are few and far between. A recent and very important discovery has been made in the dating of parietal art (cave painting) in Iberia. “Art” as we would currently define the word is associated with the cognitive abilities, but a number of decorative schemes appear to date to the later Mousterian which requires revolutionary rethinking of this concept. Hoffman et al. [1] have ascribed red ochre geometric designs, hand stencils and painted speleothems in three cave sites (La Pasiega, Cantabria; Maltravieso, Extremadura and Ardales, Andalucia) a date of 64.8 ka. More typical examples of Mousterian, ochre use are deposits found at Fumane Cave in Liguria, Italy. Peresani et al. [26] report an ochre coated fossil shell (*Aspa marginata*) possibly worn as a personal ornament in deposits dating from 45 to 48 ka. The fossil is sourced from a low-iron clay, implying that the ochre coating was intentionally applied.

It is generally accepted that migration out of Africa occurred c. 70 ka, and rapidly spreading eastwards throughout Asia and Oceania and reaching Europe after ~50 ka. These people brought with them a knowledge of the technology of ochre processing and we see a blooming of sophisticated artistry from 40 to 30 ka. In the Far East, Pitarch-Martí et al. [27] have analysed red-stained, ostrich shell beads from the 31 ka Shuidonggou Locality 2 site and found them to be coated with a red ochre composed of hematite with impurities of feldspars, micas and clays. An important site in the Northern Territories of Australia is the Purnulbura rock shelter where there is evidence of processing of both local and imported red ochres continually from 32 ka up until the present day [20]. However, it is in western continental

Europe that Palaeolithic parietal art is perhaps best known (although cave art is not limited to this region, [22]). During the period of ~35–12 ka we see an expansion of the Palaeolithic palette to include black and this is discussed in more detail below. However extensive red ochre deposits are available in the French and Spanish landscapes to furnish cave painters with more the sufficient materials, those precise provenance regions have not been identified [28,29].

The Upper Palaeolithic is particularly associated with so-called ochre burials, particularly so in regions where parietal art does not exist. One of the earliest of these is the Red “Lady” of Paviland (26 ka, [30]; Figure 2) in South Wales, UK and also remarkable is the double child burial at Sungir in Russia. The latter is an exceptional example of an ochre burial dated to ~24 ka [31]. In these and other similar occurrences throughout Europe, the bones are encrusted with hematite. It is likely that this is derived from ochre-stained clothing or shrouds rather than (as once thought) that the bodies were sprinkled with red ochre [30]. In the case of the Paviland burial, precise provenancing of the ochre has been possible and it was shown to be locally derived [18].



**Figure 2.** Red ochre encrusting the bones of the Red Lady of Paviland Cave, a Late Palaeolithic ochre burial. Photograph by Ruth Siddall, reproduced with permission of the Oxford University Museum of Natural History; specimen registration number Q.00001; Image ©OUMNH.

By the Neolithic, the painter’s palette had expanded considerably, and this will be discussed below. However red ochre was still an important component. A great deal of red ochre is used for domestic decoration at the 10-ka site of Çatalhöyük [32]. We see its use in complex religious architecture of Malta. Attard-Montalto et al. [33] has identified ochres derived from terra rossa soils and deposits in karstic fissures as paint materials during the unique Neolithic Temple Period of Malta (4th–2nd Millennia BC).

By the Bronze Age, the pigment was in use in Mycenaean and Minoan wall paintings [34–36], in Egyptian Art [14,37]. Ochres were in use in the far east. An unusual use as cosmetic sticks, wherein red ochres was mixed with dried cattle heart was discovered in Xiaohe Cemetery (1980–1450 BCE) in Xinjiang, China [38].

During the European Classical period we see for the first time, a clear, documented craft specialisation of painters and artists, with red ochre being considered part of the standard palette of artists and the costs of similar, so called “austere” pigments was included in the commission price of the artist, a practice that was to continue on into the European Renaissance. The Roman author Pliny the Elder reports known ochre sources and trade links, indeed much of his work referencing the Greek author Theophrastus, showing there was a continuum in use of these materials during the Iron Age and into the early Medieval period. As such, we see red ochres as standard and widely used pigments in both Etruscan and Roman painting [39–43].

At the 9th–12th Century CE buildings at the Angkor Wat temple complex in Cambodia, polychromy wall painting is uncommon and the palette relating to the early period of construction is limited to red, orange and carbon black (soot). Most walls are painted red using hematite red ochre [44]. The ochre was sourced from the surrounding laterite deposits, which are also the main building stones used for the construction of these temples.

### 3.1.2. Wads: Manganese Ochres

The obvious choice of black pigment for any society is the easily produced and high purity carbon-based black in the form of soot. Alternatively, woody plant material is easily charred (as are bones and ivory) to produce high quality black pigments. Therefore, it is astonishing to find that some of the earliest evidence of the use of black pigments, from the Mousterian of Europe are mineral blacks in the form of manganese ochre or wad [45,46]. Wad is an old English miners' term for black earths [47] which is primarily applied to manganese-rich earths but may also be applied to deposits of graphite. Wads are typically composed of complex assemblages of manganese oxide and hydroxide minerals plus or minus iron oxides [9]. Provenance of wads has proven to be hugely problematic as they are poorly recorded in the geological literature and not well-recognised in the landscape. Nineteenth century sources [48] described workable deposits of pigment-grade wad in Devon, Somerset and Derbyshire in the UK. Heyes et al. [45] report "blocs" of manganese dioxide earth with clear use-wear from sites in France. This substance also has properties which make it useful in fire-lighting and so it was not necessarily used in this context as a pigment. Sources of manganese oxide ochres are known from the French Massif Central [45].

Roldan et al. [12] have identified both manganese oxide black pigments as well as charcoal on a series of painted, portable "plaquettes" excavated at Parpalló Cave in SE Iberia, dating from between 26 and 11 ka using Energy Dispersive XRF (EDXRF). In Middle to Upper Palaeolithic parietal art in the caves and abris of France and Iberia, created by anatomically modern humans, used a palette of primarily red ochre, very minor yellow ochre and black. These cave paintings are the most well-known manifestation of ice-age art. Developments in radiometric dating in the early 21st Century allowed for precise radiocarbon dates to be made of charcoal fragments included in the painted surfaces. Although assumed to fall in the Magdalenian Period (12–17 ka) which is chronologically accurate for Lascaux, Niaux and Altamira and Ekain Caves, Valladas et al. [49,50] have shown that comparable painting schemes were created as early as 29–35 ka at Chauvet Cave, with a continuum of painting (and perhaps retouching of paintings) in the intervening 20,000 years at a large number of cave sites. Black pigments have been analysed by Emile Chalmin and co-workers and are published in a series of articles [51–54]. Charcoal was used as a black pigment in parietal art, but mainly for drawing outlines. Black paint fills have been identified as containing manganese oxide pigments and wad "crayons" have been excavated from several caves. Due to these phases being opaque, PLM is an inappropriate technique for the characterisation of many black pigments, and analyses were therefore confirmed by TEM, XRD, IR and Raman spectroscopy and SEM/EDX. The manganese minerals pyrolusite, romanechite, hollandite, cryptomelane, todorokite, manganite, hausmannite, nsutite, ramsdellite and groutite have been determined from the Magdalenian (17–12 ka) sites of Lascaux, Ekain, Gargas, Labastide, Combe Sauniere [51,54] and Roucadour [55]. There is no evidence to suggest that these wads were burned prior to use [53].

Provenance of these minerals is also problematic as wad sources are poorly described and composed of complex mixes of mineral phases. Identification of phases such as groutite and nsutite in these western European paintings have been highlighted as the first occurrence of these mineral phases in the regions. A note of caution is required in the interpretation of such data. To ascribed rarity and therefore novelty to such discoveries is unwise. This is unlikely to be the case. The range of known *comparanda* is simply an artefact of the available geological and mineralogical literature. From the point of view of a field geologist, there is little reason to focus on this level of detail in the analysis of small-scale mineral deposits.

Using Raman spectroscopy, Sepúlveda et al. [56] identified manganese oxide pigments in Epipalaeolithic to Neolithic (10–3.7 ka) Chile. The Chinchorro hunter-gathers used a manganese black composed of hollandite and cryptomelane for the painting of mummy wrappings and manganite, pyrolusite and cryptomelane were found in rock art from the Tangani and Pampa el Muerto Highlands. These were provenanced to Los Pumas in the Atacama Desert. In Argentinian Patagonia,

Wainwright et al. [57] identified manganese oxide blacks at the 9 ka rock art sites of Cueva de las Manos and Cerro de los Indios.

Evidence of manganese oxide black pigments in Iron Age art is scarce. Kakoulli [58]) has identified pyrolusite in Roman wall paintings at Nea Paphos in Cyprus. The main pigments used from this period onwards were carbon-based blacks, soots and chars.

Extensive discussion of the use of manganese oxide black as slips, paints and glazes in the literature on archaeological ceramics which is well beyond the scope of this paper. Manganese oxide minerals encountered in paintings are summarised in Table 1.

**Table 1.** Manganese oxide and oxide hydroxide minerals encountered in pigments.

Name	Formula	Crystal System
Cryptomelane	$K(Mn^{4+}_7Mn^{3+})O_{16}$	Monoclinic
Groutite	$Mn^{3+}O(OH)$	Orthorhombic
Hausmannite	$Mn^{2+}Mn^{3+}_2O_4$	Tetragonal
Hollandite	$Ba(Mn^{4+}_6Mn^{3+}_2)O_{16}$	Monoclinic
Manganite	$Mn^{3+}O(OH)$	Monoclinic
Nsutite	$(Mn^{4+}, Mn^{2+})(O, OH)_2$	Hexagonal
Pyrolusite	$Mn^{4+}O_2$	Tetragonal
Ramsdellite	$Mn^{4+}O_2$	Orthorhombic
Romanechite	$(Ba, H_2O)_2(Mn^{4+}, Mn^{3+})_5O_{10}$	Monoclinic
Todorokite	$(Na, Ca, K, Ba, Sr)_{1-x}(Mn, Mg, Al)_6O_{12} \cdot 3-4H_2O$	Monoclinic

### 3.1.3. Yellow Ochre

Yellow ochres, which are either rich in goethite ( $FeO(OH)$ ) or the jarosite-group minerals, are apparently uncommon in works of art prior to the later Neolithic. However, as the palette expanded beyond red and black, yellow ochre became a standard artists' material and particularly the use of goethite-rich yellow ochres became temporally and globally common. Occurrences are too abundant to cite, but significant uses of this pigment are summarised below.

Wainwright et al. [57] have found goethite yellow ochres at the 9 ka rock art sites of Cueva de las Manos and Cerro de los Indios in Argentina. Goethite has also been identified in rock art in Southern California [59]. Both goethite and jarosite ochres have been found in Egyptian painting from the Old Kingdom to the Ptolemaic period [14,60–63]. Wong et al. [64] have shown that the yellow background to the paintings in the Tomb of Tutankhamen in the Valley of the Kings (Tomb KV 62) are goethite yellow ochres. In the northern Mediterranean, goethite is recognised from Minoan and Mycenaean Art [34–36], Macedonian tomb paintings [65] and goethite ochre has been analysed on Hellenistic terracotta figurines [66] and for painting the skin of a 4th Century BCE marble statue of a male youth by Abbe et al. [67]. Yellow ochre was one of the “austere” pigments of Pliny’s palette. Goethite yellow ochres have been found across the Roman Empire in all contexts [41–43,68–71].

Stodulski et al. [72] have identified goethite-rich ochres at 6th Century CE Persepolis and Holakooei and Karimy [73] have found goethite ochres in early Islamic wall paintings in Central Iran, and Gebremariam et al. [74] have found goethite yellow ochres on Christian wall painting in Ethiopia. In China, goethite ochre is used at the Tang Dynasty Li Shimin painted tomb [75]. Goethite ochres were used at the Bhimbetka rock shelters in India [76].

The jarosite group minerals (jarosite;  $KFe^{3+}_3[SO_4]_2(OH)_6$ , natrojarosite;  $NaFe_3[SO_4]_2(OH)_6$  and hydronium jarosite;  $[H_3O]Fe^{3+}_3[SO_4]_2(OH)_6$ ), themselves part of the alunite supergroup, are globally common but comparatively poorly described in the geological literature, leading to the misapprehension that jarosite group minerals are “rare” when encountered in the analysis of works of art and on archaeological artefacts. Indeed, jarosite ochres are locally abundant and their bright lemon-yellow colour makes them readily attractive to people prospecting for pigments. The author has collected almost pure jarosite ochres from locations as diverse as Sia Copper Mine, Cyprus and

Kimmeridge Bay on the South Coast of England. The discovery of jarosite in meteorites derived from Mars has sparked more recent geological interest in these minerals and their petrogenesis in supergene environments and in association with mine waste [77–80]. Jarosite group minerals are readily distinguished from goethite using PLM due to the former's low birefringence and platy crystal morphology and are differentiated using Raman spectroscopy [61,81].

Dutrisac et al. [77] claims that jarosite group minerals were being exploited at Rio Tinto in Spain from 1200 BCE. Jarosite yellow ochres have been identified on painted objects from the 9 ka site of Takarkori, Libya by di Lernia et al. [82] and jarosite has also been detected in Australian Aboriginal rock art in the Kimberley region [83,84].

Jarosite was first recognised as a mineral pigment in Egyptian contexts and it is in art of this region that the pigment is best known [60,61,85], leading its use to be considered as a local specialisation. The discovery of jarosite in Roman and Middle Eastern contexts to have led to this pigment being interpreted as an Egyptian import. However, identifications are still not particularly common; hydronium jarosite has been identified amongst Roman painting materials at Pompeii [40] and jarosite and alunite are used in yellow paints on wall paintings from the Early Islamic (9th–11th Century CE) site of Nishapur in Iran [86]. It is likely that reanalysis of some yellow earth pigments generically described as “yellow ochre” may transpire to be composed of jarosite group minerals.

### 3.2. Green Earth

Green earths or *terres vertes* are grey green to blue green pigments derived primarily from the minerals celadonite ( $K[Mg,Fe^{2+}]Fe^{3+}[Si_4O_{10}][OH]_2$ ) and glauconite ( $[K,Na][Mg,Fe^{2+},Fe^{3+}][Fe^{3+},Al][Si,Al]_4O_{10}[OH]_2$ ). These two minerals are indistinguishable using most available analytical techniques, however, Ospitali et al. [87] have been able to differentiate these minerals using Raman spectroscopy. In addition, the paragenesis of these minerals is associated with different geological environments. Celadonite is produced through the alteration of basaltic rocks, whilst glauconite is derived from marine clays and sandstones (greensands). Provenancing of green earth pigments will therefore require a knowledge of the geology of the region in which the pigment was obtained. The terminology of green earth pigments, their components and occurrence in works of art is reviewed by Grissom [88]. Green earths were and are the most readily available pure green pigments and as such are known globally in painting. Wainwright et al. [57] found green earth pigments used in paintings at the rock art sites of Cueva de las Manos and Cerro de los Indios in Patagonia, Argentina. These sites were in use from 9 ka up until the historical period. Also in the Americas, green earth is used at the Chumash rock art site of San Emigdio in southern California [59] and celadonite green earths have been used in Tsimshian and Haida art [89].

Green earth is widely used in Roman wall painting [40,41,70,71,90–92]. Linn [43] has found green earth mixed with yellow ochre and the synthetic blue pigment Egyptian Blue at Cesarea Maritima. Perez-Rodriguez et al. [93] have found green earth (possibly a glauconite and celadonite mixture with chlorite) in wall-paintings at the Seville Alcazar. Gutman et al. [42] have found celadonite green earths at Emona in Slovenia. Debastiani et al. [94] found green earths, sometimes brightened by mixing with yellow ochre or malachite at various sites in Germania Superior (northern Switzerland, southwest Germany and east France).

The colour green features prominently in the Buddhist frescoes in the caves at Ajanta, Maharashtra, India which were painted on lime- and mud-plasters from the 2nd Century BCE to the 6th Century AD [95]. Singh & Arbad [96] have reported that the sole green used is a green earth, derived from altered basalt, suggesting that celadonite is the main mineral (although the authors report glauconite; it is not recorded which techniques were used for identification).

### 3.3. White Earths

White earth pigments include those made from deposits of chalk, kaolinite, diatomite and gypsum. We should also include the rare calcium magnesium carbonate huntite in this group. White earths

have been used directly as pigments but also have been used as extenders to bulk out pigments, as grounds for painting, as substrates for organic dyes used as so-called lakes (i.e., a dye precipitated onto an inorganic substrate) and in complex pigments such as Maya Blue which is discussed below. Microscopy is an essential analytical technique in identifying white earths, and especially those rich in, or largely composed of microfossils such as diatomite and chalk. In these cases, stratigraphic provenance may be identified from micropalaeontological analysis.

### 3.3.1. Calcite and Gypsum

Calcium carbonate ( $\text{CaCO}_3$ ) and calcium sulphate whites (including gypsum;  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , anhydrite;  $\text{CaSO}_4$  and other hydration states of calcium sulphate) are universally used in all cultures globally both for grounds and for white pigments. Identifications may simply refer to them as such or indeed just as calcium-based white (which does not differentiate calcite and gypsum). The phrase “calcium carbonate white” encompasses a wide range of possible pigment materials including natural geological pigments derived from chalk or ground vein calcite, limestone or marble, but also includes pigments made from biogenic minerals such as oyster shell, coral and avian eggshell. These varieties can only be distinguished by morphology using microscopy [9]. Calcined calcite and gypsum, applied as limewash and plaster of Paris are also not uncommonly encountered; and are used as media for wall-painting and frescoes.

Gypsum and calcite are used as white pigments in rock art by the Australian Aboriginals and the Chumash Indians of Southern California [59,84]. Holakooei et al. [86] have identified white pigments used at the early Islamic site of Nishapur in Central Iran to be composed of calcite or gypsum. Chalk and other calcium carbonate whites are common in Roman painting [41]. Chalk is used as a white pigment in the Lindisfarne Gospels (8th Century AD; [97]).

### 3.3.2. Huntite

Huntite ( $\text{Mg}_3\text{Ca}[\text{CO}_3]_4$ ) was first described as a mineral in the mid 20th Century [98], however it has been used as a white pigment for at least four millennia. Yavuz et al. [99] have described this mineral's paragenesis in shallow lacustrine environments in Turkey, where huntite, intercalated with dolomite, has developed on a basement composed of dolomites and ultrabasic rocks. Yavuz et al. [99] describe the huntite in the Yalvaç-Yarıkkaya Basin as being distinctive and noticeable in the stratigraphic succession of otherwise dolomitic marls because it is “extremely white”. This observation is important in such a deposit being attractive to people procuring pigments. Huntite was frequently used in Ancient Egyptian painting, and identification of this phase, using a broad range of techniques (including PLM, XRD and Raman spectroscopy), are increasing [61–63,100–102]. Wong et al. [64] have shown that both the grounds and the white paint used on the Tomb of Tutankhamen are composed of huntite. The source of huntite in Egypt is so far unknown to modern geologists, but it was clearly well known in Antiquity. The pigment is less well recognised in northern Mediterranean contexts. Maravelaki-Kalaitzaki & Kallithrakas-Kontos [103] have identified huntite as a white pigment and mixed with Tyrian Purple (dibromoindigotin) on Hellenistic terracotta figurines from Crete. Aliatis et al. [70] report huntite from a Roman pigment pot at Pompeii.

Holakooei & Karimy [73,104] have identified huntite as the main white pigment used to paint the interior of 8th–9th Century CE mosques in central Iran. The use of huntite as a pigment in the Yazd region of Iran is common and the mineral is known to occur in the region [105]. Huntite has also been identified in rock art in Aboriginal Australia [84].

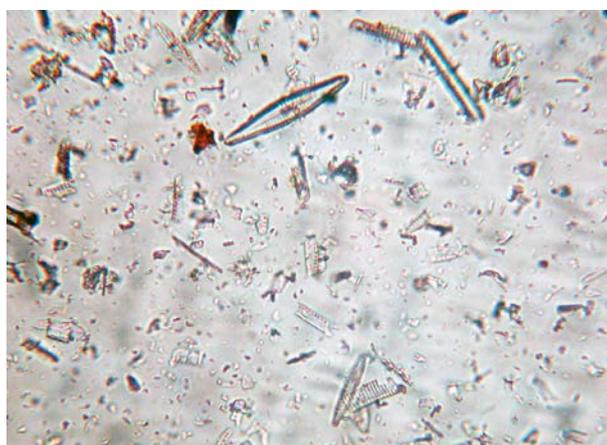
### 3.3.3. Kaolinite

China clay, or kaolinite ( $\text{Al}_2[\text{Si}_2\text{O}_5][\text{OH}]_4$ ) is a white primary clay which was similarly attractive in outcrop as a pigment. It is locally abundant in association with the hydrothermal alteration of granites and acid volcanoclastic rocks. Despite this, it is not widely recorded as yet as a pigment in its own right. Kaolinite has been used as a white pigment and as an extender in red hematite ochres in

Australian Aboriginal art, especially in the extensive rock art of Arnhem Land and Queensland [84]. Oliveira et al. [106] have identified white kaolinite used as a white paint and hematite-kaolinite mixtures in red paint analysed in Neolithic barrows (tumuli) in northern Portugal.

### 3.3.4. Diatomite and Diatomaceous Earths

Diatomaceous earths form in primarily freshwater lacustrine environments and are preserved after periods of aridity or tectonic uplift (see [107–109]). These silica-rich sediments are frequently pure white and friable, superficially resembling chalk and are therefore attractive as white pigments, fillers and substrate for organic lakes. Diatomite can only be securely identified using microscopic techniques. It was recorded used as in 1st Century CE Roman pigments by Augusti [90] at Pompeii. Also, at Pompeii, Walsh et al. [40] have found diatomite used as an inorganic substrate for an unidentified orange-coloured organic dye in pigment containers (Figure 3). It is likely that diatomaceous earths were more widely used but have not been identified due to an over-reliance on chemical and spectroscopic analytical techniques.



**Figure 3.** Diatomite used as a substrate for an orange organic dye in a 1st Century AD pigment from Pompeii.

### 3.3.5. Other White Minerals as Pigments

He et al. [110] report mixtures of gypsum and the lead sulfate ( $\text{PbSO}_4$ ) mineral anglesite in 7th–10th Century CE wall paintings at the Thousand Buddha Grotto site in Guangyang. It is possible that the anglesite was a synthetic phase which can be produced by heating galena [9]. The processes associated with the corrosion of lead were used to manufacture a range of opaque, synthetic white pigments which are structurally analogous to the lead carbonates cerrusite and hydrocerrusite from the Iron Age onwards.

### 3.4. Blue Earths

In the New World, Northwest Pacific Coast artists have been using a standard and fixed palette of red, black, blue and green for at least the last 2000 years [89], derived from minerals collected in their local environment. Red ochre, carbon blacks and green and blue earths are used. Celadonite in this context appears to be the main component of green earths. The blue earth is the mineral vivianite ( $\text{Fe}^{2+}_3[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$ ), an iron phosphate hydrate known to form authigenically in peat bogs and occasionally known as “blue ochre”. Ancheta [89] has documented vivianite’s use in Tlingit, Haida and Coastal Salish art and Fienup-Riordan [111] describes the procurement and use of vivianite by the Yup’ik people of southern Alaska from Nelson Island. Elsewhere in the Pacific region, this mineral has been recorded used as a pigment and for tattoo ink by the Maori of New Zealand

where Hamilton [112] stated the mineral was obtained from the decay of Moa (*Dinornis* sp.) bones. In Papua New Guinea [113,114] vivianite is used locally by the Wiru people of the Southern Highlands for painting masks. In the old world, vivianite is poorly recorded in archaeological contexts, but it is very likely that more identifications of this unusual pigment are made in the near future. It has been identified in Medieval painting in France and several discoveries of vivianite have recently been made in a number of easel paintings from the historical period [9,115].

Table 2 summarises the minerals encountered in earth pigments.

**Table 2.** Red, yellow, green, white and blue minerals encountered in earth pigments.

Name	Formula	Crystal System
Hematite	Fe <sub>2</sub> O <sub>3</sub>	Trigonal
Goethite	FeO (OH)	Orthorhombic
Jarosite	KFe <sup>3+</sup> <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	Trigonal
Natrojarosite	NaFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	Trigonal
Hydronium jarosite	(H <sub>3</sub> O)Fe <sup>3+</sup> <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	Trigonal
Glauconite	K(Mg,Fe <sup>2+</sup> ) Fe <sup>3+</sup> (Si <sub>4</sub> O <sub>10</sub> )(OH) <sub>2</sub>	Monoclinic
Celadonite	(K,Na)(Mg,Fe <sup>2+</sup> ,Fe <sup>3+</sup> )(Fe <sup>3+</sup> ,Al)(Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	Monoclinic
Calcite	CaCO <sub>3</sub>	Hexagonal
Huntite	Mg <sub>3</sub> Ca(CO <sub>3</sub> ) <sub>4</sub>	Trigonal
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	Monoclinic
Kaolinite	Al <sub>2</sub> (Si <sub>2</sub> O <sub>5</sub> )(OH) <sub>4</sub>	Triclinic
Diatomite	SiO <sub>2</sub>	Amorphous
Vivianite	Fe <sup>2+</sup> <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	Monoclinic

### 3.5. Coal and Hydrocarbon Blacks

Despite their obvious talents as opaque, velvety, black pigments, asphaltites and coals are poorly recorded amongst black pigments. This may partly be because they are difficult to identify using the techniques applied to the identification of inorganic minerals. Gas chromatography mass spectrometry (GC-MS) is an essential technique required to characterise, identify and provenance these materials [116]. There is some evidence for the use of “asphalt” in the ancient near east in a variety of contexts from adhesives and waterproofing agents in boats. These materials are sourced from this region [117,118] and it is known the solid asphaltites can be ground and used as pigments as well as liquid bitumens. The use of asphalt in works of art has been reviewed by Bothe [119] and these materials (including humic-earth based pigments) are much more prevalent in artworks of the historical period [9]. Connan et al. [120] have reported bitumen-painted pottery from the Late Neolithic site of Tell Sabi Abyad in Syria. From the bronze age, bitumen was in use to paint the hulls of boats [121] and similarly it was used in model boats such as the Gurob Ship Cart, an early toy boat dated to c. 1256 BCE [122,123]. Mazzochin et al. [68] reported Roman use of coal as a pigment at Talanta.

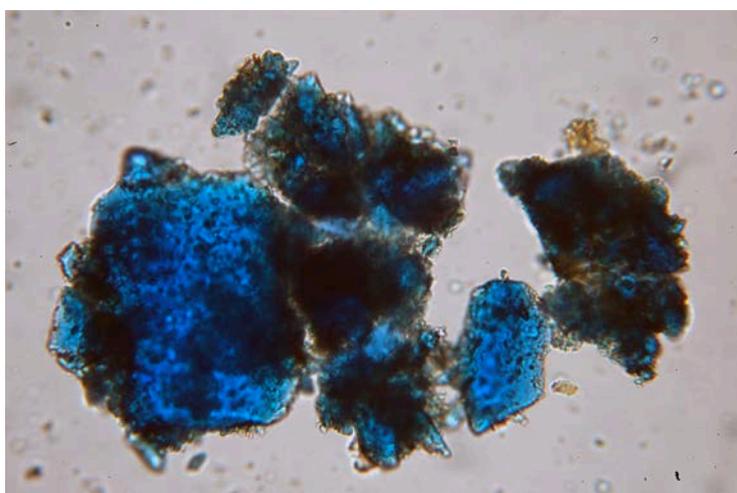
## 4. Blue and Green Mineral Pigments

Of all the colours of mineral pigments, the blues break all the rules. Not only are they some of the more rarer minerals, but many of them, some of which are synthetic analogues of naturally occurring minerals, are silicates. They also include the most intense pigment known, ultramarine. Blue pigments have been considered precious throughout art history. As primary colours they can be only represented by pure, single phases and not mixtures. Vivianite (described above), though locally abundant is not widely available and appears to have been used in restricted cultural contexts. Blue has always been a valued colour and great lengths and the application of technology has gone into its procurement. In addition to the valuable mineral pigments and their synthetic analogues, the organic dye indigo has been used in painting and it should be noted that so called “optical blues”, which can be very convincing to the eye, can be produced through mixture of waxes and carbon black [59].

#### 4.1. Malachite and Azurite

The copper carbonate hydroxides, malachite ( $\text{Cu}_2[\text{CO}_3](\text{OH})_2$ ) and azurite ( $\text{Cu}_3[\text{CO}_3]_2(\text{OH})_2$ ) are well-known and relatively common green and blue minerals. These minerals are well defined by spectroscopic methods [7] and are distinctive under PLM [9]. Natural minerals are considered to be used throughout the archaeological period. Synthetic malachite and azurite, pigments called green and blue verditers, have been produced since the early Medieval period. Although chemically and structurally analogous to the naturally occurring minerals, they are simply distinguished using PLM; verditers precipitate as 10–40  $\mu\text{m}$  spherulites of fine, radiating crystallites. Eastaugh et al. [9] and Gettens & FitzHugh [124,125] provide reviews of the use, production and identification of both natural and synthetic forms of malachite and azurite. Aru et al. [126] have studied azurite in potential and known pigment sources in Europe, Siberia and North Africa, and found that natural impurities include malachite, hematite, goethite, jarosite, cuprite, anatase, rutile, cerussite, calcite and graphite and the pigment analyst should be minded that these may occur within pigment contexts. Malachite and azurite are difficult pigments and lose their colour when finely ground. This may account for their relative rarity in archaeological contexts.

Very early evidence of the use of ground azurite as a blue pigment has been found at the Neolithic, Central Anatolian site of Çatalhöyük (Figure 4). The site is well-known for its wall paintings, but there is no evidence as yet that azurite was used as a pigment for painting. It is only encountered in graves, particularly in female and infant burials, perhaps suggesting the pigment's significance as a treasured cosmetic material. Çamurcuoğlu's analyses show the azurite from burial contexts dating around and just after 6700 BCE to be of very high purity and coarsely ground with particles of 40–100  $\mu\text{m}$ . Rare malachite was also discovered within the same archaeological contexts [32].



**Figure 4.** Azurite from Neolithic funerary context at Catalhöyük, Turkey. Plane-polarised light (PPL). 250 $\times$ , field of view is  $\sim$ 0.5 mm. Photomicrograph by Ruth Siddall and Duygu Çamurcuoğlu.

Attributions of azurite in Ancient Egyptian painting are few and disputed [127]. Malachite was used in Ancient Egyptian painting and particularly in the context of female “green-faced” coffins from the 26th Dynasty (Saite Period, 7th Century BCE) as identified by Scott [127]. Moussa et al. [128] have found malachite and hydrocerussite (possibly an admixture rather than a naturally occurring impurity) at the 6th Century CE Church of the Virgin in Wadi El Natrun, Egypt.

Malachite has been identified in wall-paintings and paint pots at Pompeii by Walsh et al. [40] and Aliatis et al. [70]. Malachite mixed with green earths and yellow ochres has been identified at Roman sites in southern Germany [94]. Malachite and Egyptian Blue were found by Aloiz et al. [129] and Stodulski et al. [72] at Persepolis and Pasargadae.

Malachite has always been an important pigment in Asian painting. Jin et al. [130] has identified malachite used as a pigment in post-firing decoration of ceramic vessels excavated from the Han Dynasty Yangqiaopan Tombs in Shaanxi Province, China. The Mogao Grottoes, located near to Dunhuang in Gansu Province, China consist of 492 painted caves dating from the 4th to 14th Centuries AD. Zhang et al. [131] have analysed Tang Dynasty (618–907 AD) wall paintings and discovered malachite, azurite and atacamite using SEM-EDS and IR spectroscopy. Sultan et al. [75] have also identified malachite in Tang Dynasty polychromy architecture and wall paintings.

Garcia Moreno et al. [132] working at Calakmul, Mexico, have found malachite and pseudomalachite as decorative paint on ceramic vessels and head-dresses, however these minerals were absent from wall paintings.

Azurite appears from the 9th Century and malachite from the 11th Century on illuminated manuscripts in the UK and western Europe, and azurite is used on 10th Century manuscripts from northern Spain [97,133]

#### 4.2. Copper Salts: “Salt Green”

In addition to malachite and azurite, a number of copper salts and related compounds are found within the supergene enrichment products associated with copper mineralisation and with the corrosion of copper and bronze metals [134]. These are attractively and brightly coloured in hues of blue and green and would have been noticeable in the landscape and forming on the surfaces of metal artefacts exposed to the elements. The name *viride salsum*, “salt green” was coined by the 12th Century author Theophilus [135] and has a generic application to (synthetic) copper salts.

Pigments that fall into this group are primarily copper trihydroxychlorides and copper-zinc trihydroxychlorides. Despite being relatively unfamiliar compounds to mineralogists, these phases are becoming increasingly commonly encountered in works of art [134,136] and it is difficult to describe these minerals from a petrological point of view without substantial reference to the growing literature characterising the occurrence of these minerals in cultural heritage. The main phases encountered are the  $\text{Cu}_2\text{Cl}(\text{OH})_3$  polymorphs atacamite, paratacamite, clinoatacamite and botallackite [9,137]. Alejandre & Marquez [136] have found these phases along with copper-zinc trihydroxychlorides (zincian paratacamite) on a 16th Century wall painting in the Chapel of Mercy, Cadiz, Spain, confirmed via microscopy, XRD, SEM and FT-IR. The origin of these pigments remains poorly understood, however these authors present three possible origins; (1) that these are naturally occurring minerals; (2) that these phases are the alteration products of malachite/azurite or the synthetic copper acetate compounds generically known as verdigris [134,138]; or (3) that these phases originate from the corrosion of copper, bronze or brass in the presence of chloride salts and acid conditions [134,139,140]. Intentional synthesis of such copper salts has been poorly reported (in contrast, methods for the manufacture of other synthetic pigments, including verdigris, organo-copper greens and lead pigments etc. using corrosion are well documented throughout history from the Classical period onwards [9]. Importantly, Alejandre and Marquez [136] found cuprite within their “salt green” pigment samples, although this could be an impurity in a natural-mineral derived pigment, it is not in itself an alteration product and perhaps indicates a synthetic origin of these pigments. Theophilus describes a method of coating copper sheets with a mixture of honey and sea salt (NaCl), which after a few months corrodes to form salt green, in this case, atacamite. This method has been successfully tested by Scott [134], Nord and Tronner [141] and Fulcher [63].

The presence of these phases as pigments has been confirmed by a range of techniques [134,136,142] and their widespread occurrence, both geographically and temporally requires that more work is needed to fully understand their origins. It is possible that copper and copper-zinc trihydroxychlorides were procured from all three possible sources described above.

Gimenez [143] reports an identification of a copper trihydroxychloride which he ascribes to atacamite, on polychrome coffin of the Ptolemaic—Romano-Egyptian period, perhaps produced as the degradation of Egyptian Blue (see below). This analysis is tentative and based on the green

colour and the presence of chlorine. However, it should also be noted that the synthetic pigment Egyptian Blue is common across the Mediterranean ancient world and is extremely stable. Numerous other identifications of atacamite as a pigment are known from Egypt [144,145] and Nubia [63]. It is assumed, given a strong track record of innovation in creating green pigments from copper and bronze in Ancient Egypt, that these atacamite pigments were manufactured. In Greece, Brecolaki et al. [146] have identified paratacamite and antlerite ( $\text{Cu}_3[\text{SO}_4][\text{OH}]_4$ ) on 4th Century BCE funerary couches at Amphipolis.

In South America, Sepúlveda et al. [147], have identified atacamite and clinoatacamite on rock paintings and atacamite contained as a powder, in pure form, in leather pouches, from the Late Intermediate and Late periods (900–1550 AD) of Northern Chile. Here in the Atacama Desert, the type area for atacamite, there is preliminary evidence that mineral atacamite and clinoatacamite, derived from copper ores and specifically selected for its shade of colour, was being used as a pigment.

Numerous analyses of painted artefacts and wall paintings from China have identified the presence of copper trihydroxychlorides, indeed in some instances, indicating a preference of the use of this pigment over malachite. Occurrences have been reviewed by Yong [148] from the North Dynasty (386–581 CE) to the late Qing Dynasty (1840–1911 CE). Early uses of atacamite as a pigment may have been natural or due to the degradation of malachite. He et al. [110] have identified malachite and atacamite mixtures as well as pure atacamite green pigments at the Thousand Buddha Grottoes in Guangyuan (7th–10th centuries CE), and Wang & Wang [149] also found pure atacamite used more frequently in painting than malachite at the Mogao Grottoes of Dunhuang, perhaps indicating that atacamite was cheaper or more readily available than malachite. Yong [148] postulates that from the 10th Century CE, and possibly much earlier, copper trihydroxychlorides were synthesised from the corrosion of bronze using salt and vinegar; a process for which Yong is able to cite documentary evidence. Botallackite has also been identified at the Buddhist Zhongshan Grottoes in Shaanxi, China, dating to the 11th Century CE [150].

In Early Medieval Europe, atacamite has been identified in numerous wall paintings in churches, dating from the 13th–16th Centuries in Sweden, and particularly, in Gotland where it is found in association with malachite [141]. Once again, the origin of this mineral is speculative, perhaps imported from natural sources in Russia, or alternatively synthesised from corroding copper sheets in the presence of chlorine.

#### 4.3. Brochantite

Brochantite ( $\text{Cu}_4[\text{SO}_4][\text{OH}]_6$ ) is a copper sulphate hydroxide with an attractive emerald green colour, which can form naturally in the supergene enrichment of copper ores and can be included amongst the “salt greens”. It has been identified on Tibetan Thangka paintings, perhaps produced as an alteration of malachite [151]. This pigment has also been recognised in historical period painting in Europe [152].

#### 4.4. Tyrolite

Stodulski et al. [72] also identifies tyrolite ( $\text{Ca}_2\text{Cu}_9[\text{AsO}_4]_4[\text{CO}_3][\text{OH}]_8 \cdot 11\text{H}_2\text{O}$ ), a copper arsenate hydroxide, using XRF, XRD and FT-IR spectroscopy, in green paints from the 6th Century CE Achaemenid sites of Persepolis and Pasargadae in Iran. This was found in mixtures with other blue and green minerals. Mineral tyrolite is known to be found in Iran, but this analysis, not replicated by later authors working on the same site, needs further research to confirm veracity.

#### 4.5. Veszelyite

Veszelyite, a copper-zinc phosphate hydrate ( $[\text{Cu,Zn}]_2\text{Zn}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$ ), has been reported by Garcia Moreno et al. [132] at the Classic period (AD 250–800) site of Calakmul in Mexico. A green pigment was found on funerary masks and related objects in association with jadeite and serpentinite mosaic work; the pigment has been mixed with lime mortars. The vezelyite was very pure and

ground into angular fragments of particle size range 5–20 µm. Garcia Moreno et al. [132] speculate that this mineral was specifically chosen as it is a very good colour match for the jadeite. Veselyite has been identified at La Esperanza Mine in Puebla, Mexico, however further work is required to ascertain the source of this unusual and unexpected mineral pigment. This important discovery may require the reinterpretation of other green minerals in Mayan Classic period art identified as malachite on the basis of the presence of copper alone.

#### 4.6. *Lapis Lazuli, Lazurite and Ultramarine*

The rock lapis lazuli, which is rich in the dark blue, sulfur-bearing h uyne phase lazurite ( $\text{Na}_6\text{Ca}_2[\text{Al}_6\text{Si}_6\text{O}_{24}][\text{SO}_4, \text{S}, \text{S}_2, \text{S}_3, \text{Cl}, \text{OH}]_2$ ) is probably the best known of all mineral pigments. However, lazurite, more often referred to as ultramarine, is not archaeologically significant. Although the stone was used for decorative purposes in Central Asia, the Near East and Far East, technology to extract lazurite was not developed until the 6th Century CE, then taking another four centuries to reach the palettes of western European artists. Because of its relative rarity, and from documentary sources we know that all lapis lazuli sourced in Antiquity was derived from a single location, the mines at Sar-e-Sang in Badakhshan, Eastern Afghanistan. Here lapis lazuli is developed in skarns hosted in calcite-dolomite marbles [153]. The extraction of lazurite from lapis lazuli leaving aside other blue minerals such as sodalite as well as carbonates and pyrite is no simple task, and natural sources of ultramarine often contain trace amounts of these minerals as impurities, which are readily observed using PLM. Another rule is broken with this pigment; even with the use of natural lazurite, the term “ultramarine” is generically used to describe this pigment in both natural and synthetic forms. Synthetic varieties (not developed until 19th Century; [9]) are referred to, simply, as “synthetic ultramarine”. The first recognised uses of ultramarine pigment were in the Sogdian States in the 1st Millennium CE. However, Brysbaert identifies what she calls an “enigmatic” occurrence of ground lapis lazuli used in a purple pigment found at the mainland Greek Bronze Age site of Gla [154]. The mineral was identified using Raman spectroscopy and the purple paint was created from red ochre (hematite) mixed with blue pigments. Further analysis would be needed to confirm this as being more than a one-off discovery.

Certain and obvious large-scale use of lapis lazuli and lazurite as a pigment occurs in artworks associated with the Sogdian states located in central Asian between the Oxus and Jaxartes Rivers. The Sar-e-Sang mines lay on the borders of Sogdian territories, and Sogdia was located on the trade network of the Silk Roads. Unfortunately to date, few analyses have been made on Sogdian wall painting materials and techniques. Gettens [155] identified an early use of lapis lazuli as a pigment on the 6th–7th Centuries CE wall paintings at Bamiyan in modern Afghanistan. Impressive schemes of wall paintings in the Hall of the Ambassadors at the site of Afrasiab (Afrasiyab), near Smarkand in Uzbekistan, show processions of dignitaries on a background of deep blue lazurite pigment [156]. These have been ascribed a date of 660 CE. Holakooei & Karimy [73] have identified lazurite in blue pigments in early Islamic period mosques in Central Iran dating to the 8th–9th Centuries CE.

Ultramarine pigment moved eastwards along the Silk Road from an early date. Singh & Arbad [96] report its use at the Ajanta Grottoes in Central India, which have been dated from the 2nd Century CE—6th Century BCE, though these paintings have been retouched subsequently. It is not clear whether this discovery is indeed a very early use of lapis Lazuli in the East or if it relates to a later period when this pigment was more established. Liu et al. [157] have reported lazurite used as a post-firing, decorative pigment on ceramic figurines representing Sogdians found in Wei Dynasty Tombs in Luoyang. These date to the early 6th Century CE. The 7th to 10th Century (Tang Dynasty) Thousand-Buddha Grotto in Guangyuan are decorated with wall paintings. These have been analysed using a range of analytical techniques, including PLM [110]. Lazurite has been discovered as the main blue pigment phase. Lazurite (and indeed synthetic ultramarine) has also been identified at the Mogao Grottoes at Dunhuang representing a long history of trade along the Silk Roads [131].

Apart from the tentative identification made by Brysbaert [154], ultramarine is not seen in Europe until the early Mediaeval Period. In Britain it has been identified on Anglo Saxon and European manuscripts dating from the late 9th Century through to 11th Century [97].

#### 4.7. Maya Blue

Maya Blue is an intense, opaque turquoise blue or blue-green, which was used in Pre-Columbian South America by the Mayans, Toltecs, Mixtecs and Aztecs for wall paintings, decorating ceramics, and on textile and documents [158]. It was in use from the 8th Century CE to the 16th Century [159]. It is not strictly a mineral pigment as the blue colour is imparted by the plant dye indigo. The blue dye is precipitated onto white clays, primarily palygorskite and sepiolite. This process involves heating the indigo and the clay at 150 °C for two days (for more detail, see Sanchez del Rio et al. [160]). The structure and chemistry of the resulting complex compound is described from a mineralogical point of view by Chiari et al. [161]. Identification using Raman Spectroscopy is straightforward as the clay-dye complex produces double peaks, specifically at 1578–1595  $\text{cm}^{-1}$  [159,162]. Mayan Blue has been characterised on a number of different objects by Kleber et al. [158] and identified on wall-paintings at Calakmul, Mexico by Garcia-Moreno et al. [159].

#### 4.8. Synthetic Blue Green and Purple Pigments

Early synthetic inorganic pigments which are important in archaeological contexts are described here. These include the blue, green and rare purple silicate phases Egyptian Blue and Egyptian Green synthesised from the 3rd Millennium BCE in Egypt, and the related compounds (though unrelated technologies) Han Blue and Han Purple developed from the 3rd Century BCE in China [9].

Egyptian Blue, Han Blue and Han Purple exhibit remarkable near-infrared luminescence properties, allowing for non-destructive confirmation of minute quantities of these pigments on artefacts. These properties and their analyses were discovered by Giovanni Verri and were tested on a range of painted materials. Visible induced luminescence (VIL) has become a routine technique for identifying these important synthetic pigments and methodology, equipment and analyses are described in a series of papers [163–167]. Although not observed in historical period art, these pigments have been synthesised in the 20th Century and are once again commercially available from fine art suppliers [168].

#### 4.9. Egyptian Blue

Egyptian Blue is the most important blue pigment used in North African, European and Middle Eastern archaeological contexts. It is a calcium copper silicate, analogous to the rare naturally occurring mineral cuprorivaite ( $\text{CaCuSi}_4\text{O}_{10}$ ). Cuprorivaite has never been recognised as a pigment in its own right, though erroneously and misleadingly, many authors have described occurrences of synthetic Egyptian Blue as cuprorivaite. Egyptian Blue is easy to synthesise, and the process was described by the Roman author Vitruvius. Copper (or bronze) filings are heated in a clay crucible in the presence of quartz sand (or diatomite), calcium carbonate and a soda or potash flu to temperatures of 950–1000 °C. Glass phases (“frits”) are produced at lower temperatures. Numerous experimental work has determined the synthesis of this pigment [134,169,170] and analytical techniques can elucidate variations in manufacture, for example major element mapping can indicate whether sodic or potassic fluxes were used, and whether the copper source was copper oxide (tenorite), copper or bronze [9]. Egyptian Blue, as noted above, it is now readily commercially available. Egyptian Blue is encountered in Egyptian wall painting from the 4th Dynasty onwards into the Roman Period [37,64,100,101,167]. Siddall [122] has reported Egyptian Blue from the Gurob Ship Cart (c. 1256 BCE). It is clear that Egyptian Blue was considered a trade item during the Mediterranean Bronze Age, cakes of the pigment were found on the late 14th Century BCE Uluburun Wreck [171]. Egyptian Blue is found in frescoes from Minoan and Mycenaean sites in Greece, which are dominated by a palette of red, yellow, black, white and blue [34–36,172–176].

Within the context of Egyptian Blue pigments in the Aegean Bronze Age, it is worth examining the attribution of the sodic amphiboles glaucophane and riebeckite also used as blue pigments with these contexts and mixed with Egyptian Blue. Mark Cameron made assumptions that blue-grey pigments observed in Minoan wall painting were in part composed of glaucophane [177]. Arguably, if glaucophane had been used as a pigment anywhere, then the Aegean region would have been the most likely region. This mineral is readily available in the very pure glaucophane schist of the Cycladic Blueschist Unit of the Hellenides and they outcrop on the islands of Siphnos and Syros and elsewhere in the Cycladic LTHP metamorphic zone, and indeed, the author has made a workable blue-grey pigment, very similar in colour to vivianite, from Siphniot glaucophane. In addition to Knossos, glaucophane has been proposed as a pigment at Thera and Pylos [173–175]. However, in all these studies, the presence of glaucophane has been predicated based on semi-quantitative major element analyses made by SEM-EDS. PLM has not been applied in these studies and this technique would prove successful in differentiating glaucophane from Egyptian blue and other silicates based on the obvious optical properties of these minerals, primarily pleochroism. Brysbaert et al. [176] did not detect glaucophane in their analyses of Aegean Bronze Age painting using laser-induced breakdown spectroscopy (LIBS).

Occurrences of Egyptian Blue in later Greek Classical and Hellenistic art are widely attested by Riederer [169,178], Kakoulli [172], Gassanova et al. [66] and in Achaemenid Iron Age architecture by Stodulski et al. [72] and Aloiz et al. [129]. By the Roman Period, manufactories of the pigment outside Egypt had become established and are documented by contemporary authors. We know from Vitruvius that the pigment developed a trade name as Vestorian Blue after Vestorius set up a factory in Pozzuoli on the Bay of Naples. Davy found cakes of “blue frit” in the ruins of the Baths of Titus which his analyses proved were of the same composition as the blue pigment found in the wall paintings [5]. The pigment is used throughout the gamut of Roman painting [40,42,43,71,91]. In the early medieval period, Riederer has identified late occurrences of Egyptian Blue in 9th Century AD Christian wall paintings [169]. Egyptian Blue becomes less frequently used in the historical period, although it is not absent in artists’ palettes.

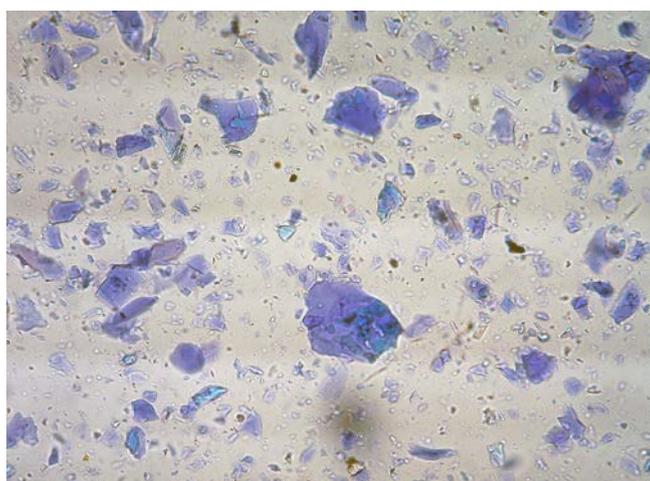
#### 4.10. Egyptian Green

A green pigment analogous to the pyroxene (para)wollastonite ( $\text{CaSiO}_3$ ) plus a copper-bearing glass phase was apparently intentionally produced by varying the manufacture processes for Egyptian Blue and subsequently known as Egyptian Green [9,134,179,180]. This pigment has been described from late 3rd millennium (New Kingdom) BCE Egyptian and Mesopotamian contexts. There appears to be an association of this pigment to the Egyptian Amarna Period; evidence of “factories” have been found at Tell El Amarna and Hatton et al. [181] have analysed cakes of “green frits” from this site. Ullrich [182] has identified Egyptian Green on the bust of Nefertiti, also excavated at Tell el Amarna and it has been found in the Tomb of Tutankhamen by Wong et al. [64]. Pagés-Camagna and Colinart [180] have identified this pigment on a number of objects from the Old Kingdom (3rd Millennium BCE) to the 21st Dynasty (10th Century BCE).

#### 4.11. Han Blue and Han Purple

Blue and purple pigments, termed Han Blue and Han Purple by Fitzhugh & Zycherman [183,184] are extremely similar in composition and manufacture to Egyptian Blue, though the two production processes developed in isolation. These are barium copper silicates (The blue phase is  $\text{BaCuSi}_4\text{O}_{10}$  and the purple,  $\text{BaCuSi}_2\text{O}_6$ ; Figure 5). Han Blue is chemically and structurally analogous to the naturally occurring mineral effenbergite [185]. Han pigments have been identified on artefacts from the Warring States Period (475–221 BCE) and the Han Dynasty (208 BCE–220 CE). These phases have particularly distinctive optical properties and are readily identified by PLM [9] and also by XRD [186]. Liu et al. have also demonstrated that lead fluxes ( $\text{PbCO}_3$ ) were used to control the synthesis of Han Purple over Han Blue.

Han Blue and Purple have been identified on the Terracotta Warriors, the armies associated with the burial of the First Emperor of China Qin Shi Huang in 210–209 BCE by Bouherour et al. [187], Thieme [188] and Liu et al. [186]. Xia et al. [189] have identified, using PLM and Raman spectrometry, both Han Blue, Han Purple and mixed pigments on a range of objects including, wall paintings, pigment sticks and paint pots, ceramic figurines and beads. Jin et al. [130] have also identified Han Purple as a pigment used as post-firing, painted decoration on ceramic vessels from the Han Dynasty Yangqiaopan Tombs in Shaanxi Province.



**Figure 5.** Han Purple. A modern pigment preparation supplied by Kremer Pigmente. PPL, 400×, field of view 0.25 mm. Photomicrograph by Ruth Siddall.

Table 3 summarises the blue minerals encountered as pigments including green and purple variants and synthetic analogues of naturally occurring minerals.

**Table 3.** Blue and green mineral pigments and synthetic analogues important in archaeological contexts.

Name	Formula	Crystal System
Malachite	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$	Monoclinic
Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$	Monoclinic
Atacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	Orthorhombic
Paratacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	Trigonal
Clinoatacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	Monoclinic
Botallackite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	Monoclinic
Antlerite	$\text{Cu}_3(\text{SO}_4)(\text{OH})_4$	Orthorhombic
Brochantite	$\text{Cu}_4(\text{SO}_4)(\text{OH})_6$	Monoclinic
Tyrolite	$\text{Ca}_2\text{Cu}_9(\text{AsO}_4)_4(\text{CO}_3)(\text{OH})_8 \cdot 11\text{H}_2\text{O}$	Orthorhombic
Veszelyite	$(\text{Cu,Zn})_2\text{Zn}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	Monoclinic
Lazurite	$\text{Na}_6\text{Ca}_2(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4, \text{S}_2, \text{S}_3, \text{Cl}, \text{OH})_2$	Cubic
Egyptian Blue	$\text{CaCuSi}_4\text{O}_{10}$	Tetragonal
Egyptian Green	$\text{CaSiO}_3 + \text{Cu glass}$	Triclinic + amorphous
Han Blue	$\text{BaCuSi}_4\text{O}_{10}$	Tetragonal
Han Purple	$\text{BaCuSi}_2\text{O}_6$	Tetragonal

## 5. Red, Yellow and Orange Mineral Pigments.

Red and yellow ochres are the most abundant and most widely used red, orange and yellow pigments encountered in archaeological contexts. However, the arsenic sulphide and mercury sulphide minerals were used for brighter colours. These locally abundant but globally uncommon phases were prized and their distribution indicates that they were considered important trade commodities.

### 5.1. Orpiment, Realgar and Pararealgar

The arsenic sulphide phases, orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\alpha\text{-As}_4\text{S}_4$ ) and pararealgar ( $\text{As}_4\text{S}_4$ ) have been widely used as pigments, as testified by the name of the  $\text{As}_2\text{S}_3$  phase orpiment, being derived from the Latin for “golden pigment”. Arsenic sulphide minerals form in association with volcanic sublimates around fumaroles [190] and in association with gold mineralization [191,192].

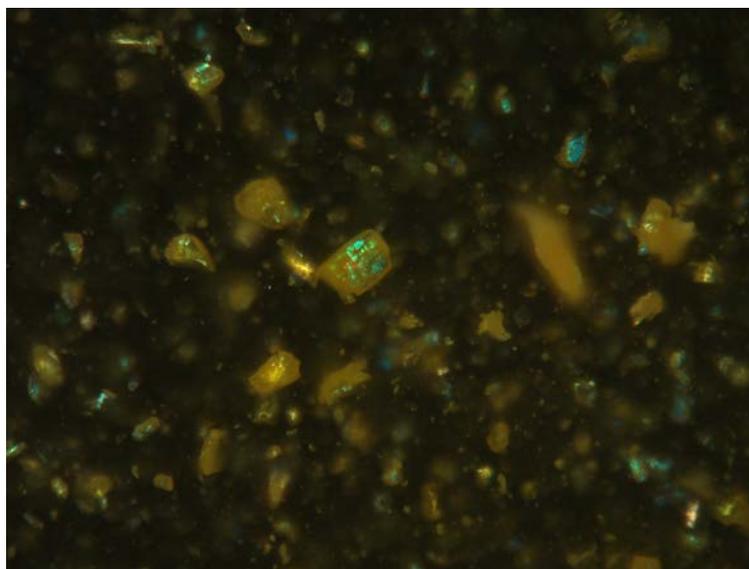
These pigments were not without their problems; they are highly toxic, not particularly common in the geological environment, and hard to grind down to appropriate particle size and unstable. Orange realgar converts to yellow pararealgar on exposure to light, and orpiment similarly converts to white arsenic ( $\text{As}_2\text{O}_3$ ) in oxygen-rich environments [193–195]. However, these minerals were prized for their intense red and golden-yellow colours and were considered to be valuable, “florid” pigments on artists palettes of the Roman period, according to the contemporary author Pliny the Elder. Their geological rarity led to early manufacture of these phases, and most occurrences of arsenic sulphide minerals in historical period artwork are synthetic analogues. Grundmann & Richter [196] review the arsenic sulphide phases, their synthesis and occurrence in painting.

Orpiment and realgar are used in Ancient Egyptian painting from the New Kingdom to the Roman Period in all contexts [60]. The Greek author Herodotus claimed that orpiment was found on the Island of St John (Zabargad, also Topazios) in the Red Sea. Composed predominantly of peridotites [197], St John is an unlikely provenance for the orpiment frequently seen in Egyptian painting, nevertheless this attribution has erroneously proliferated through the literature, without the support of modern field observations. It is likely that arsenic sulphide phases are abundant in the regions of gold mineralisation in the Eastern Desert, and it is more likely that this bright yellow mineral, and the associated phase realgar, was procured as a by-product of gold mining or was brought into Egypt from the Middle East via trade. The pigments have been found in many aspects of Pharaonic Egyptian painting. Uda et al. [100] have found orpiment, mixed with goethite, on wall paintings in the Malqata Palace from the reign of Amenhotep III (18th Dynasty, 1390 BCE). Olsson et al. [198] have found orpiment on Books of the Dead painted on to papyrus. Bonnizzoni et al. [199], using major element analyses only, obtained using pXRF, have indicated that a yellow orpiment pigment is used on a coffin of the 26th Dynasty (6th Century BC) and Dawson et al. [200] report the occurrence of orpiment on coffins and funerary art from the Middle Kingdom onwards, noting that it was used to symbolised gold and also that the shard-like crystals imparted a sparkle to the painted surface. Rowe et al. [201] and Vandenabeele et al. [202] have identified orpiment on Ptolemaic and Romano-Egyptian period cartonnage mummy masks, using PLM, XRF and Raman microspectroscopy.

Outside Egypt, Gebremariam et al. [74] have identified orpiment on 12th Century CE wall paintings at Yemrehanna Krestos Church, Ethiopia. These analyses, made using pXRF are based on major element analyses and the observation of colour. Orpiment and realgar are widely used across Asia. Li et al. (2009) have identified a mixture of orpiment and realgar in a yellow paint on a 5th Century CE lacquer screen. Nöller & Hahn [203] have identified copious use of orpiment or synthetic  $\text{As}_2\text{S}_3$  on 6th to 13th Century CE illuminated manuscripts from Central Asia, found at various sites along the Silk Road. “Vergaut” is a green pigment made from mixing orpiment and indigo. It has been identified by Clarke [97] on a number of Anglo-Saxon and early Mediaeval manuscripts, including the Lindisfarne Gospels. Pure orpiment is also used on the same manuscripts for bright yellows. It was also being used in Visigothic Spain for manuscript illumination [133].

Realgar (Figure 6), due to its instability when exposed to light is less frequently encountered, and the occurrence of pararealgar may be interpreted as orpiment using chemical techniques which are unable to differentiate these phases. The two phases are readily distinguished using PLM, orpiment usually exhibiting high relief, striated, bladed crystals with extreme birefringence and pararealgar tends to be anhedral with anomalous blue-green interference colours. Realgar is fairly well-known from Ancient Egyptian funerary contexts, especially in Books of the Dead and other papyri, where long burial in darkness have preserved this pigment. McCarthy [204] has reported red ochre mixed with realgar and yellow ochre mixed with orpiment in Suemniwet’s Tomb in Thebes

(c. 1430 BC). At Tell El-Amarna, pigment samples excavated by Sir Flinders Petrie and now in the Manchester Museum included a sample of realgar seemingly intentionally mixed with pararealgar [14]. Realgar occurs on painted coffins from the New Kingdom onwards, but it is not a commonly used pigment in these contexts [200]. Calza et al. [205] have identified realgar on a Romano-Egyptian period mummy case in the National Museum, Rio de Janeiro, Brazil.



**Figure 6.** Natural realgar prepared as a pigment supplied by Kremer Pigmente and viewed in cross-polarised light (XPL). The image shows the typical anomalous green interference colours exhibited by this mineral; 400×, field of view is 0.25 mm. Photomicrograph by Ruth Siddall.

Orpiment and pararealgar have been recorded at the Macedonian Tombs (4th Century BCE) of Phoinikis near Thessaloniki, Greece, using  $\mu$ -XRF and SEM-EDS [65].

Both orpiment and realgar were identified by Li et al. [206] on a Chinese 5th Century CE lacquerware painted screen, excavated from a burial complex in Shanxi Province, using a combination of microscopy, FTIR, Raman spectroscopy and XRF.

As a word of caution, orpiment and white arsenic ( $\text{As}_2\text{O}_3$ ) washes and “arsenic soaps” were often used as an early conservation measure to protect documents, textiles and taxidermy from attack by insects, the poisonous nature of the pigment deterring vermin [207]. Analysts need to be aware of such treatments when identifying pigments on textiles and manuscripts.

## 5.2. Cinnabar

Cinnabar ( $\text{HgS}$ ) is a bright red mineral which is locally abundant in Almadén, Spain, a number of localities in south Central China and several other regions, including notably several sources in Central Europe and the Near East [191,208]. The Spanish and Chinese localities are historically significant for the exploitation of cinnabar as a pigment, and it is not surprising that early uses of this mineral in artists palettes are associated broadly with these regions. Petrogenetically, cinnabar is associated primarily with hydrothermal mineralisation in the presence of marine black shales (see Hazen et al. for a review of mercury mineralisation and geologic settings [208]). Cinnabar is found in both vein and exhalative settings and large crystals may be encountered (Figure 7). Cinnabar produces a bright red, opaque paint, with a luminosity above that of even the best red ochres. After ultramarine, cinnabar was the most valuable, and therefore prestigious, pigment on the market. Cinnabar is readily synthesised. Traditional, so called “dry-process” manufacture involved heating native mercury and sulfur together in a clay vessel over a strong heat. The resulting product is known as vermilion however the reality is that dry-process vermilion is indistinguishable from the natural mineral, and therefore it is hard to

determine when this process was first used. As native mercury is as valuable and rare as cinnabar, there was little difference in value between the two materials. Nevertheless, the procurement and trade in cinnabar and its synthetic equivalent, vermilion are important in global art histories from the Neolithic onwards.



**Figure 7.** Cinnabar crystals in association with carbonates from Hunan Province, China. Photograph by Ruth Siddall.

“Iberian Cinnabar” sourced from the mercury mines at Almadén in south central Spain was well known to the 4th Century BCE author Theophrastus, indicating that a Mediterranean-wide trade in this mineral as a pigment was established by the Hellenistic period. Nevertheless, in practice, such a trade in this important red pigment may have been in place much earlier. There is abundant evidence for cinnabar being used from the Neolithic onwards. In the Iberian Peninsula, cinnabar pigments have been reported from several Neolithic and Chalcolithic sites. Emslie et al. [209], report mercury poisoning probably associated with cultural use of cinnabar at the Neolithic site of Perdigões, near Evora in Portugal. Direct evidence comes from Rogerio-Candelera et al. [210] who have excavated cinnabar, identified by Raman spectroscopy and XRD, in burial contexts from the Chalcolithic period (3rd Millennium BC) at Valencina de la Concepción, near Seville. The authors do not attempt to Provenance the source of cinnabar but Almadén, lying some 200 km to the NE is a likely source. The placing of this pigment in a burial setting indicates it was probably a high-status material. In Central Europe, cinnabar is found at 6th Millennium BCE Neolithic Vinca Culture sites, both on painted objects and stored in pots. The pigment was probably obtained from deposits near Belgrade, 300 km to the north of the main site of Plocnik [211].

At the eastern end of the Mediterranean, cinnabar was used in wall painting at Çatalhöyük in the 7th millennium BC. Cinnabar deposits are known from the hinterland of the Konya Plain and although provenance studies have not yet been made, it would seem that their proximity makes this the most likely source [32].

Cinnabar is relatively rare in Egyptian and Near Eastern Art until the Greek and Roman Periods. Bonizzoni et al. [199], have identified a red pigment on an Ancient Egyptian, 26th Dynasty coffin as cinnabar using pXRF. Cinnabar was used copiously by the Iron Age Iberian Culture (6th–1st Centuries BC for wall paintings and the post-firing decoration of ceramics [212]. Cinnabar, probably procured from the mercury mines of Almadén, was important in the European Classical world for the production of documents, where red lettering, “rubric”, signified important text. Cinnabar has been identified used for text on the Dead Sea Scrolls (late 5th Century BCE–4th Century AD; [213]). Alarmingly, given its poisonous nature, cinnabar has been recorded in Roman, Punic and Egyptian cosmetic preparations by Ribechini et al. [214] and Huq et al. [215]. Cinnabar was widely used in Roman wall-painting and was a valuable, perhaps the most valuable, pigment on the artists palette. We see it in the Emperor Nero’s

lavishly decorated Golden House (Domus Aurea; Clementi et al., 2011) and at Pompeii's Villa of the Mysteries [90] and for spectacular, bright red walls at Thamusida, Morocco [41]. It has been identified in many other Roman contexts [43] and Siddall and Piovesan (*in prep*) have found frequent occurrences of red hematite ochre and cinnabar mixtures in red paints in Romano-British wall painting. In near eastern contexts, cinnabar has been found on Achaemenid (550–330 BC) architecture at Persepolis and Pasargadae in Iran [72,129].

In the Far East, cinnabar has been on artists palettes since the Neolithic [216]. Cinnabar has also been identified at the Zhongshan Grottoes [150], in Tang Dynasty polychromy architecture [75]. Cinnabar is an important colourant in the production of Chinese lacquerware; the oldest known lacquer bowl dates from 7000 BCE and this material is still in production. Li et al. [206] have identified cinnabar in a 5th Century CE lacquerware screen using a combination of microscopy, FTIR, Raman spectroscopy and XRF.

A 3500-year history of the extraction of cinnabar for use as a pigment has been recorded in Peru has been detected in the form of mercury pollution in lake-sediment cores in the vicinity of the Huancavelica mercury deposit. Evidence of mercury mining dates as early as 1400 BCE and the mineral was used as a pigment by the Pre-Colombian Chavin and Inca States and into the historical period [147,217].

In the European early Medieval period, cinnabar has been identified in a late 10th century CE Visigothic manuscript from northern Spain and on 11th Century Anglo-Saxon manuscripts [97,133].

## 6. Mineral Blacks

Following extensive Palaeolithic use of manganese oxide pigments, the majority of black pigments used in Antiquity were carbon blacks; soots and chars. Stibnite is often rumoured as being used in cosmetics (kohls) but analyses have not proven this attributions. Ribechini et al. [214] report a few instances of galena found in traces of Egyptian and Roman cosmetics. Other documented uses of mineral blacks are rare. Wagner et al. [218] have found lead in black inks used in an Egyptian Book of the Dead and postulated that galena may well have been a component. Plattnerite ( $\beta$ -PbO<sub>2</sub>) has been identified as a black pigment by Holakooei and Karimy at an 8th–9th Century Mosque near Yazd in Central Iran and has been sourced to nearby deposits in the Darreh Janjir Mine near Taft [73]. Plattnerite also occurs as a decay product of the synthetic pigment white lead [9], however Holakooei & Karimy identified plattnerite used as a black paint in bands in contrast to a white ground composed of huntite. They do not record the use of white lead as a pigment.

Table 4 summarises the yellow, orange, red and black minerals encountered as pigments in archaeological contexts.

**Table 4.** Yellow, orange, red and black mineral pigments.

Name	Formula	Crystal System
Orpiment	As <sub>2</sub> S <sub>3</sub>	Monoclinic
Realgar	$\alpha$ -As <sub>4</sub> S <sub>4</sub>	Monoclinic
Pararealgar	As <sub>4</sub> S <sub>4</sub>	Monoclinic
Cinnabar	HgS	Trigonal
Galena	PbS	Cubic
Plattnerite	$\beta$ -PbO <sub>2</sub>	Tetragonal

## 7. Conclusions

Throughout Antiquity, artists' pigments were dominated by the earth pigments, (iron) ochres, wads (manganese oxide ochres) and chalk, and palettes were similarly limited by colour to red, yellow, blacks and whites. Arsenic and mercury sulphides were used where available to produce bright yellows, oranges and reds. Copper salts were widely used as blue and green pigments and lapis lazuli-derived ultramarine became important from the 6th Century AD onwards as a blue pigment.

Mineral blues and greens were relatively rare and therefore expensive trade commodities, and the importance of crystalline, synthetic inorganic pigments cannot be ignored. Blue, green and purple silicates were manufactured in Egypt from the 3rd Millennium BC and in the east from the 3rd Century BC. As these phases are structurally analogous to naturally occurring minerals, it is important that they are considered within the range of “minerals” used here, in order to highlight the fact that they are synthetic. The range of materials used as pigments in Antiquity is well understood and the discovery of new phases used as pigments is a relatively rare event. The identification of veszelyite in Classic period Mexican art [132] is an exception and a recent example of the discovery of a new mineral pigment phase. This case study is also important in its thoroughness. It demonstrates that major element analysis alone can lead to assumptions and hence spurious identification of pigments; multi-technique analyses, including optical techniques are essential in determining the character of pigments.

However, it should also be stated that too much focus should not be put on the discovery of an unusual or apparently geologically rare mineral within a pigment mixture. Earth pigments particularly are complex and too much weight should not be put on the occurrence of rare phases, such as the manganese oxide hydroxide groutite in wads from Central France. The absence of a discussion of these minerals in the geological literature is simply an absence of analysis rather than evidence of the non-existence or rarity of a mineral in a particular region. As such, the analyses of archaeological pigments have much to contribute to regional mineralogical surveys.

Nevertheless, there is still much work to do. The occurrence of copper salts such as atacamite [219], ubiquitous in archaeological painting, globally, and yet apparently uncommon as a mineral in the geological environment, requires further research. A method to fingerprint ochres and identify provenance and processing techniques would also be extremely useful.

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