REVIEW

Pigments—Iron-based red, yellow, and brown ochres

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Abstract
Natural Fe-bearing ochres ranging in color from yellow to deep red and brown abound on earth's crust. Quite often, ochres can be used for pigmenting purposes upon little or no processing, and, hence, the pertinent materials have been widely employed for decorative and artistic purposes since the dawn of prehistory; ochres have also found medicinal applications. This paper offers an overview regarding the range and composition of the available natural ochre pigments, their origin, properties, and potential processing. In addition, the production and processing of artificial ochres is presented. The prevailing analytical techniques currently employed in ochres' identification and provenancing are also discussed, and guidelines for good practice are provided. Finally, authors offer some insight on ochres' potential applications and their limitations, while a discussion pertaining to ochres in the Greco-Roman world is also included.

Keywords Hematite · Goethite · XRD · μ-Raman · SEM–EDX · Gilding

Premise

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

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

This article is part of the Topical Collection on *Mortars, plasters and plasters and pigments: Research questions and answers*

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Furthermore, several issues concerning the degradation and conservation of mortars and plasters are addressed from practical and technical standpoints (La Russa and Ruffolo 2021; Caroselli et al. 2021).

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

Introduction

Some of the soils that cover part of the earth's crust owe their color largely to the presence of iron oxides or/and oxyhydroxides (see next for details). These earthy materials are mostly formed upon the weathering of several minerals and rocks, and, hence, apart from iron compounds, they contain small or large amounts of various other mineralogical components. The variability of iron compounds themselves and that of the accompanying minerals result in the existence of a considerable range of earths' hues, from deep purple and brown to light red and yellow (Fig. 1). Although not every colored earth is suitable to be used as a pigment, iron-based substances of pigment quality exist in uncountable sources all over the globe; hence, some pertinent artist's materials were always broadly available (Hradil et al. 2003). On the other hand, the retrieval of high-quality/ "special" pigments was occasionally required; therefore, some sources were preferentially exploited, and the relevant products were transported over long distances via commercial routes. Renowned examples include the red iron earth from Sinopi ("Σινωπική μίλτος"), a fine red earth from Armenia that was often used as a gilding substrate ("Armenian bole") and others (Helwig 2007). However, some of the most popular sources of the past have been exhausted; indicative examples include the natural red ochre from Venice and the ochres mined at the Cava delle Mazzarelle quarry in Monte Amiata (Sienna district, Italy) (Harley 1982; Manasse and Mellini 2006).

Ochres popular in the Greco-Roman world and times are considered in detail below. Some of the natural ochres of interest during later times are the following (Jolly and Collins 1980; Harley 1982; Buxbaum and Pfaff 2005):

(a) Characteristic yellow ochres are those from France and South Africa. The popular French natural yellow ochres exhibit low oxyhydroxide content (under 30wt% and even under 10 wt%). On the other hand, South African

natural yellow and red ochres exhibit very high levels of iron oxides/oxyhydroxides (40–70wt% expressed as Fe_2O_3).

(b) Characteristic red ochres are the Indian red, Persian red (especially from Hormuz), and Venetian red; also remarkable are the red ochres from Iberia (in Bilbao and South Spain or Portugal) (Gil et al. 2007), the UK (in Southwest and Northwest England and in Wales), and South Africa.

The names might indicate actual sources or key trade centers or even a traditional name that was eventually transferred to new products; in addition, some of the so-called natural red ochres are actually fired versions of natural yellow ochres. Finally, some of the names were eventually transferred to manufactured products, as, e.g., the case of Venetian red, starting from the late eighteenth century.

Available archaeological evidence supports that Fe-bearing substances have been used for pigmenting (and other) purposes during the last 300,000 years (Helwig 2007; Rosso et al. 2016; Zipkin et al. 2017). There are numerous examples of prehistoric rock paintings that have been largely executed in various shades of ochres, and the simultaneous symbolic/ritual employment of ochres by prehistoric man is also well attested (Domingo and Chieli 2021). Ochres were extensively used by ancients in the frame of various disciplines such as painting, pottery manufacturing/ornamentation, domestic decoration, and medicinal practices (Helwig 2007; Photos-Jones et al. 2018), and their extensive employment continued during medieval and post-medieval times as well (Harley 1982; Hradil et al. 2020). Today, apart from their employment in art materials (e.g., in paints, crayons, colored pencils, and pastels), natural and artificial Fe-bearing pigments are also considered important industrial materials, as they are frequently incorporated in marine and other coatings, in cement and lime mortars (as colorants), in plastics and rubbers, etc. (Helwig 2007; Buxbaum & Pfaff 2005). In addition, ochres were (and still are) extensively used as gilding substrates (in the form of red or, sometimes,

Fig. 1 Commercial ochre pigments (Kremer Pigments). From left to right: light ochre from Cyprus (Kremer code: 17000), burgundy yellow ochre (11573), Cyprus raw umber (40610), and red mine ochre (40351)

yellow boles, see next) in the frame of panel paintings/icons and woodcarving decoration (Sandu et al. 2011; Mastrotheodoros et al. 2016).

This review covers yellow, orange, red, red purplish, and brown earth pigments known as ochres (also spelled ochers) and the related pigments known as raw and burnt siennas and umbers. Note that the term "ochre" (or "ocher") stems from the Greek word "ωχρός/ochros" (pale/yellow-colored) that during antiquity denoted yellow, while red was called "μίλτος/miltos" (Caley & Richards 1956; Becker 2021). The Greek "ὤχρα" (ōchra) is the ultimate source of the current English term ochre/ocher; the corresponding Latin term is sil (/ silis, gen.), but Romans also used the Greek term (as ochra).

Gradually "ochre" gained a much wider sense and during the sixteenth century was already used indiscriminately for yellow, red, and brown Fe-bearing pigments (Hradil et al. 2003; Helwig 2007). However, due to the origin of the term, misconceptions have occasionally arisen, and, hence, some scholars have suggested alternative nomenclature for the pigments in consideration, such as "earthy pigments" and "iron oxide pigments" (Hradil et al. 2003; Helwig 2007; Hradil et al. 2020). Nevertheless, the term "ochre" (accompanied by color specification) is very often used in order to describe collectively the various Fe-based pigments that have colors in the spectrum yellow-deep red/purple-brown (see, e.g., Gettens and Stout 1966; Elias et al. 2006; Eastaugh et al. 2008; Rifkin 2012; Montagner et al. 2013; Siddall 2018) and will be used here in the same manner.

This review covers the various pigments that are based on Fe(III) oxides and hydroxides (e.g., hematite and goethite, respectively), i.e., the yellow, orange, red, red purplish, and brown earth pigments known as ochres (also spelled ochers) and the related pigments known as raw and burnt siennas and umbers. In addition, yellow pigments based on jarosites are also considered, despite the somewhat different composition of the latter Fe(III) minerals (a typical one being $KFe_3(SO_4)_2(OH)_6$; i.e., a hydroxysulfate mineral of Fe(III) and K) (Desborough et al. 2010). Besides, in view of their color and similar role of Fe(III), jarosite-based pigments are often viewed as a special type of yellow ochres both in commercial descriptions and technical literature (e.g., Siddall 2018). On the contrary, this work will not cover the black, mixed Fe(II)/Fe(III) oxide magnetite (Fe_3O_4) and the various black earths/ "wads" (or "black ochres") which are very rich in manganese (present as pyrolusite and various manganates) (Vouvé et al. 1992; Eastaugh et al. 2008).

Ochres in the Greco-Roman world

During Greco-Roman times, two out of the four colors of the "basic palette" for painting are ochres. In particular, as Pliny states (*Naturalis Historia* – NH 35.50), celebrated painters such as Apelles created immortal paintings "*ex albis Melino e silaciis Attico*, *ex rubris Sinopide Pontica*, *ex nigris atramento* (= from white [earth] of Melos and yellow ochre of Attica, from red ochre from Sinope of Pontus, from atramentum black)"; a related statement is found is Cicero (*Brutus*, 18.70). The scheme of a four-color palette is loosely related to the four element theories of Empedocles (ca. 495–435 BC) and others. Actually, there is one report (DK 31,92a) that Empedocles[1] himself referred to white, black, red, and ōchron as the four basic colors regardless if the latter theoretical scheme originates from Empedocles or someone else; the ōchron color of the scheme probably reflects the color of some reference ōchra (= yellow ochre) pigment.

During the Greco-Roman period, ochres were used in applications such as painting, architecture, medicine, agriculture (Lytle 2013), and cosmetics (e.g., "*miltō aleiphomenos*" in Xenophon's Oeconomicus, 10.5; also Homer's (Iliad, 2.637) "*miltos-cheeked ships* (= nēes, fem.)" suggests the existence of "miltos-cheeked women"; for a detailed reference to the cosmetic use of pigments, see Pérez-Arantegui 2021) and special adhesives (see, e.g., the "leucophorum" described by Pliny in NH, XXXIII.20 and XXXV.17). In addition, Herodotus reports body painting applications of red ochres in Africa (Herodotus IV.191 and VII.69). Finally, red ochre has been widely (and continuously) employed in rituals since the early periods of human evolution (see, e.g., Dubreil and Grosman 2009; Román et al. 2015; Gravel-Miguel et al. 2017; Rigon et al. 2020).

It is not possible to review herein the world history of ochre pigments which are painting materials continuously in use from Paleolithic to present times; therefore, we will limit ourselves to a systematic consideration of certain historical aspects of the Greco-Roman world ochres: a detailed account on the key Greco-Roman literature on ochres is presented in Appendix 1. One might find some gathered pertinent information in corresponding material guides, as in Lucas and Harris (1999) for ancient Egypt and in Moorey (1999) for ancient Mesopotamia.

Natural ochres: geology and mineralogy[2]

In terms of composition, the materials described as ochres correspond to earth deposits that are rich in metal oxides and/or hydroxides (oxyhydroxides, e.g., akaganéite). Although some non-iron ochres do exist (e.g., bismuth ochre, antimony ochre, nickel ochre, see Eastaugh et al. 2008), the great majority of ochres employed for pigmenting purposes

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[1] Empedocles' work is referenced according to its standard edition by Diels–Kranz 1951, 308–374 (DK 31).

[2] This part of the paper is largely based on a contribution by Dr. Y. Bassiakos (INN, NCSR "Demokritos").

are colored due to Fe(III) oxides/hydroxides. Note that the various green earths are also colored due to Fe, yet in these cases, the chromophore iron is contained in the constituting clay phases, i.e., celadonite and/or glauconite (Konta 1995). Pigment quality ochres with a Fe_2O_3 content up to 95% do exist in nature (Gettens and Stout 1966), yet most natural ochres contain variable amounts of other minerals (e.g., quartz, clays); the type and amount of the latter depend on the source of the pigments and the processing it may have undergone prior to their use (Elias et al. 2006; Helwig 2007).

Geology

Iron (Fe) is rare in its native, metal state although its ores are classified among the most abundant in the earth's crust. Red and yellow iron oxides and hydroxides in the mineralogical form of hematite and goethite are the most important and abundant constituents of the natural ochres, being used as pigments for thousands of years. Ochres have been used for several purposes: artistic, embellishing, ceremonial, body painting, and others, including medicinal practices. The earliest possible evidence for ochre exploitation seems to be at Olduvai (Tanzania, E. Africa) dating back to the Lower Paleolithic times, almost half a million years ago (Rapp 2002). More enlightening evidence comes from pieces of ochre, deliberately shaped to be used as "pencils" or "crayons" that have been found in Upper Paleolithic graves; some of them have worn-out tips, thus providing undoubted proof of use (Taçon 2004). As regards early mining of ochres, Thassos Island in N. Aegean constitutes a unique case for which underground ochre mining dating to the Upper Paleolithic has been confirmed (Koukouli-Chrysanthaki and Weisgerber 1999). At a site known as Tsines in southern Thassos, one of the earliest open-cast and underground ochre mines in Europe has been excavated, the use of which appears to have been initiated around 20,000 years ago, verified by radiocarbon dating.

Natural, Fe-based ochres may derive from all three major classes of rocks that make-up the upper earth's crust. For example, iron oxides are often formed by means of decomposition or unmixing processes on Fe-Ti oxides deriving from magmatic formations. One other phase classified along with ochres is jarosite ($KFe_3(SO_4)_2(OH)_6$). Moreover, metamorphic rocks deriving ochre is represented by decomposition of iron-rich containing metamorphosed rocks (e.g., metabasites, metamorphosed manganiferous rocks) altered by decomposition, weathering, or hydrolysate geochemical processes to iron oxides and hydroxides (Cornell and Schwertmann 2003). In addition, primary iron oxides also exist in metamorphic rocks (i.e., they were not generated after decomposition) and in hydrothermal formations, while they also form upon weathering of iron-rich ores. Note that ochres remaining close to their parent ore/rock are classified

as "primary" ones, while those that have been formed in the surface environment and were subsequently transported away from the parent deposit through, e.g., erosion and sedimentation are designated as "secondary"; the latter are often less pure than the former (Eastaugh et al. 2008).

Primary ochres forming upon the weathering of Fe-rich igneous and metamorphic rocks are of high purity and can be readily spotted (due to their intense coloration) in outcrops; examples include the inter-basaltic bole horizons that are in fact iron-rich ochres entrapped between successive basalt lava flows (Ghosh et al. 2006). However, sedimentary rocks constitute the principal sources of iron minerals, especially Fe oxides and—in a lesser degree—hydroxides that constitute most natural ochres across the continents. Many of them were formed under marine conditions; hence, they often include traces of marine fossils (Tucker 2001), and they are characterized by layered banding of iron minerals, mostly consisting of hematite or magnetite, interbedded with chert and/or microcrystalline quartz (Rapp 2002). In addition, ochreous deposits associated with clays were (and still are) commonly exploited for pigment production (Hradil et al. 2003).

Among the most important agents that account in the transformation of the Fe-based formations to ochres are the initial constituents/mineralogy of the primarily layered formations, pH, electrochemical conditions, morphological features, altitude, temperature, and water, while the climatic type and the latitude are also significant with the subtropical conditions (relatively high relative humidity and temperature) favoring the alteration processes. Besides, it has been noted that the type of iron oxide formed is largely determined by environmental conditions rather than by the structure of the parent mineral (Iriarte et al. 2009).

Finally, one shall mention two other important ochre formation processes, namely acid rock drainage (ARD) and acid mine drainage (AMD); the former occurs naturally, while the latter is linked to human mining activities. Iron sulfide minerals (e.g., pyrite) exposed to air and water can be biodegraded by biomineralizing bacteria, a complex process that leads to the precipitation of various types of Fe-rich sediments such as ferrihydrite, goethite, and jarosite (Singh et al. 1999; Máša et al. 2012). There is sound evidence indicating that pertinent ochres have been employed for painting purposes since prehistoric times (MacDonald et al. 2019).

Mineralogy

Natural Fe-based ochres constitute by far the most widespread and extensively used class of mineral pigments. Their color depends on the main compound (e.g., iron oxide or oxyhydroxide), phase (e.g., alpha vs. gamma FeOOH), their degree of crystallinity, grain size, and presence of additional phases such as clays containing minor amounts of other

cromophores (e.g., Mn) (Marshall et al. 2005; Elias et al. 2006; Helwig 2007; Dubiel et al. 2011; Montagner et al. 2013). Consider for example artificial red ochres produced through the firing (in identical conditions) of two yellow ochres; substantially different red hues might be produced as a result of different levels and/or spatial distributions of clay phases, which can affect (via definition of small subdomains) the grain size of the ferric material. Note that in general, the latter exhibits a growing grain size during firing (Mastrotheodoros et al. 2010). Also, the level of crystallinity of a new phase (e.g., hematite formed upon firing of yellow ochre) can be affected by factors such as the type and particle size of precursor, type and duration of processing steps, and the presence of potential crystallization inhibitors (Walter et al. 2001; Cornell and Schwertmann 2003, Gialanella et al. 2010; Rzepa et al. 2016; Fouad et al. 2019).

The main coloring compound of yellow ochres is α-FeOOH (goethite), while the less stable γ-FeOOH (lepidocrocite) is a rarer ochre-coloring mineral or occurs as a minor ochre phase. The main coloring mineral of red ochres is rhombohedral Fe_2O_3 (hematite or haematite); massive hematite is of a distinct dark gray and shiny appearance (Fig. 2) and was often used for the manufacturing of gilding burnishing tools (Gettens and Stout 1966). Maghemite, a red-brown γ-Fe_2O_3 mineral is less frequently employed for pigmenting purposes; for example, it occurs as a minor phase of some burnt ochres (Eastaugh et al. 2008) and is occasionally identified in red iron pigments (Helwig 2007). In addition, the poorly ordered and rather unstable ferrihydrite ($Fe_{10}O_{14}(OH)_2$) that precipitates from oxygenated Fe-rich aqueous solutions upon enzymatic oxidation induced by bacteria (waste product of their metabolism) might have also been occasionally employed as a pigment (Cudennec and Lecerf 2006; Siddall 2018). Here we shall note that the term limonite which appears occasionally in the relevant literature (e.g., Edwards et al. 2004) is in fact a generic one that corresponds to a combination of ill-to-non (or crypto-) crystalline Fe(III) hydroxides and oxides (often goethite or mixture of the latter with lepidocrocite, hematite, etc.) (Holser 1953; Cavallo and Zorzin 2008; Eastaugh et al. 2008).

On the other hand, jarosites are MM'$_3$(SO$_4$)$_2$(OH)$_6$ materials, where M is usually K (also Na, H$_3$O, etc.) and M' is Fe(III), but it can be partly replaced by Al, etc. (Basciano & Peterson 2007; Desborough et al. 2010). A jarosite can be macroscopically confused and/or used as a goethite-based pigment, but jarosites are brighter than ordinary yellow ochres and somewhat reminiscent of orpiment. Jarosite deposits are found in many places around the world, and it has been recently stated that their use as pigments was mostly of local importance (Siddall 2018). Presumably the latter statement reflects the rather limited identifications of jarosite in painting context (e.g., Wallert 1995; Salvant et al. 2018; Kostomitsopoulou Marketou et al. 2019; Marcaida et al. 2019); therefore, one must keep in mind that the presence of this particular mineral in painting samples might sometimes have been overlooked.

The color of the pure Fe(III) oxides and oxide hydroxides depends largely on grain size. According to Buxbaum and Pfaff (2005), with increasing grain size, (a) goethite shifts from green yellow to brown yellow, (b) lepidocrocite shifts from yellow to orange, and (c) hematite shifts from light/yellow red (0.1 μm) to dark violet (1.0 μm). The color dependence on grain size has been also assessed by Marshall et al. (2005) who studied in detail an assembly of ochre samples from SW UK, as well as by Mastrotheodoros et al. (2010) who examined several natural and artificial ochre samples. It might be useful noting here that the term "caput mortuum" is occasionally employed to describe artificially prepared dark violet pigments with relatively coarse-grained hematite particles (Harley 1982; Eastaugh et al. 2008). Moreover, in the case of needle-like particles, the color of the pigment is also affected by the aspect ratio of the needles, while substitution of iron cation by other elements (e.g., Mn) affects the color;
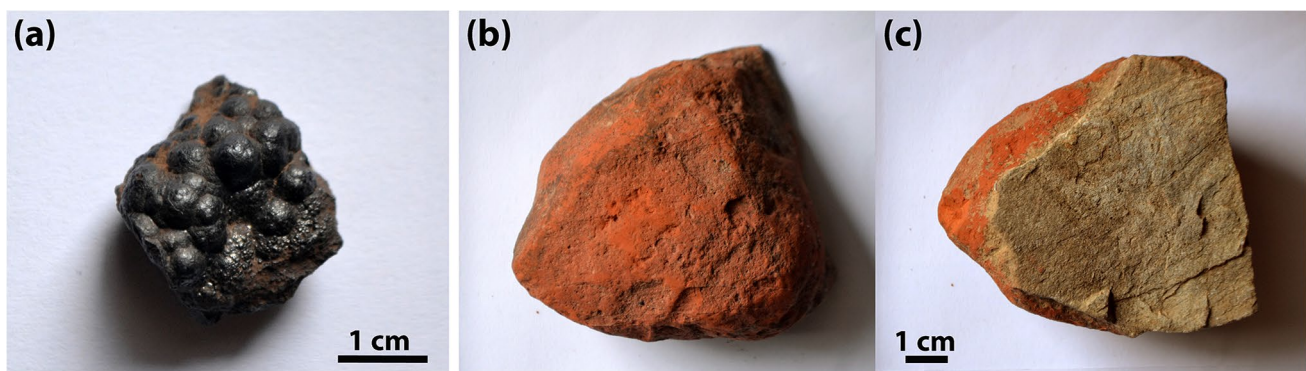

Fig. 2 **a** Botryoidal hematite specimen from Thassos Island, Greece. **b** and **c** Natural red ochre from Evia Island, Greece, on a slate substrate (**c**). Authors' collection

for instance, Mn-substituted goethite appears olive brown to blackish (Marshall et al. 2005; Helwig 2007).

In addition to oxides and/or hydroxides, natural ochres are often associated with various minerals and rocks (Fig. 2b and c) and include additional phases, such as aluminosilicates (clay phases such as kaolinite and illite), quartz, sulfates (of Ca or Ba), carbonates (such as calcite and dolomite), jarosite, sulfides, carbon, organics, and anatase (a form of tetragonal TiO_2). Evidently, the presence and amount of additional minerals/phases affects considerably the color of an ochre (Marshall et al. 2005; Dubiel et al. 2011), and Elias et al. (2006) have underlined the major role that the white charges play on ochres color. Some examples of quantified natural ochre compositions appear in Table 1 (data from Elias et al. 2006), while qualitative composition data from a wider variety of ochres are presented in Froment et al. (2008). As it is clear from Table 1, a substantial portion of the mass of natural ochres does not correspond to Fe(III) oxides and oxide hydroxides.

On the other hand, siennas and umbers (or umbras) differ from ochers mainly in that they embody a substantial amount of manganese oxides. Both these pigments are offered in "raw" (goethite based) and "burnt" (fired and, thus, hematite based) forms, and their names appear to reflect Italian toponyms (Siena (in Tuscany) and Umbria, respectively). However, in the latter case, the currently prevailing derivation is that from umbra (= shade or shadow), Latin > [terra d'] ombra (Italian) or [terre d'] ombre (Middle French). Usual descriptions of the color of all types of siennas and umbers include the term brown; the raw versions are more yellowish, and the burnt versions are more reddish and darker. While the dehydration of Fe(III) oxyhydroxides enhances darkness (and redness), one common means for the generation of dark to very dark shades is the incorporation of manganese oxides (such as Mn_3O_4 and MnO_2); particle size also affects color.

Raw siennas are largely goethite-based as regards the Fe(III) component, while the manganese oxide content usually ranges from 0.2 to 5%, yet, substantially different values are found in parts of the literature (Bikiaris et al. 1999; Genestar and Pons 2005; Manasse & Mellini 2006; Eastaugh et al. 2008; Nicola et al. 2016). Siennas usually exhibit compositions "between" those of yellow ochres and umbers, especially as regards manganese content. Some siennas are described alternatively as umbers with a low to moderate manganese content, while some other siennas are approached as yellowish to brown ochres, usually with an enhanced manganese content. In addition, raw siennas tend to contain more Fe(III) (in the form of goethite) than the common yellow ochres, while they also contain some peat and/or organics and are warmer than common ochres having a comparable hue. Reference siennas are those of Tuscany, but some of the best sources are already exhausted or near exhausted by now; related, yet inferior as regards hue (at least according to some purists) earths are found in Sicily, Sardinia, France, Germany (Hartz mountains), and elsewhere. Siennas are yellow–brown in the raw state, while burnt siennas exhibit, largely as a result of hematite formation, a warm, red-brown hue (Church 1915). In the area of Tuscany, the locally mined raw siennas are further divided into yellow earths, brown boles, and intermediates (Manasse and Mellini 2006). Church (1915) synopsizes some data as regards the composition of siennas. Fe(III) content, expressed as Fe_2O_3, is 46 to 60% (w/w), while manganese, expressed as MnO_2, is 0.6 to 1.5%. Manasse and Mellini, who have studied a broad range of South Tuscany raw siennas (both yellow earths and brown boles), have found a high "Fe_2O_3" content (54 to ca. 70% w/w), a low manganese content (0.0–0.7% w/w, when expressed as MnO), and a substantial presence of arsenic (from ca. 1 to ca. 10% when expressed as As_2O_5). Arsenic is found adsorbed on the surface of goethite nanoparticles, and it is also present in South Tuscany samples from 1867 and 1915; no clear trend between arsenic content and color was detected despite pertinent earlier suggestions.

Typical umbers contain between 3 and 30% (w/w) manganese oxides and hydroxides and 45–70% iron(III) oxides and oxyhydroxides (Genestar and Pons 2005; Eastaugh et al. 2008; Nicola et al. 2016; Fuster-López et al. 2016). When the manganese oxide content is in excess of $50 \pm 15\%$ (with the exact limit affected by the Fe_2O_3 and white mineral fractions), the products are black or brownish blacks and are called wads (Eastaugh et al. 2008; Siddall 2018). Reference umbers are those of Cyprus (see Table 2); in the raw state, the latter are deep brown with an olive green hue. Umbers

Table 1 Examples of composition (expressed as phases, molar concentrations, %) of yellow (Y) and red (R) ochres; values adapted from Table 2 of Elias et al. (2006). Y1, Y2, and R2 come from Vaucluse (South France), Y3 from Madras (India), R1 from Italy, and R3 from Sweden

Ochre	Hematite	Goethite	Aluminosilicates	Calcite	Quartz	Gypsum + anhydrite
Y1	0.0	3.0	26.9	0.0	70.1	0.0 + 0.0
Y2	0.0	28.2	14.2	0.0	15.6	0.0 + 0.0
Y3	0.0	65.0	23.1	11.9	0.0	0.0 + 0.0
R1	8.3	1.2	1.1	0.0	0.3	89.1 + 0.0
R2	30.5	0.0	27.5	4.0	38.0	0.0 + 0.0
R3	36.4	0.1	1.1	4.4	49.6	0.0 + 8.4

Table 2 Compositions (expressed as oxides (wt%); reported Fe_2O_3 includes goethite) of two raw umbers from Troulli quarries (Cyprus); based on data from Jolly and Collins (1980) (loi = loss on ignition)

Sample	Fe_2O_3	Mn_3O_4	SiO_2	Al_2O_3	CaO + MgO	SO_3	loi
Umber 1	44.8	3.0	20.0	8.7	3.7	0.1	18.4
Umber 2	44.4	15.4	9.4	5	0.7	?	16.8

somewhat similar to the Cypriot ones are found in Syria and other Middle East areas. Burnt umbers are dark brown with a red undertone (Buxbaum and Pfaff 2005).

Raw versions with some natural organics (which is usual for umbers and occasional for siennas) might fade slightly upon continuous exposure to sunlight for a number of years (Church 1915). Siennas and umbers have a long history of use in painting, though near discontinuities are also known; for example, umbers were already used during prehistory but resurfaced in the European painting at around 1500 (Thompson 1956) and soon after appeared versions of their current name. On the other hand, sienna-type pigments were already used by Romans, and their use was continued in later times, while their current name (< terra di Siena, It.) became standardized in the eighteenth century (Helwig 2007). Sienna-type and umber-type materials are also possibly sometimes hidden in past references to ochers (e.g., possibly in Pliny, NH XXXIII.56 and in Cennini, XLV) or other products.

Selection and processing of natural ochres

The spotting of potential natural ochre sources seems like a rather straightforward task due to the distinct colors of the pertinent earthy materials. However, empirical testing methods such as scraping of ochre specimens on hard rocks and in situ testing of grinding properties are simple means of a preliminary appropriateness evaluation. Moreover, it is crucial to assess the color of an earthy substance after its complete drying, as the humidity content affects considerably the color of granular/powdered substances (Konta 1995; Monnard et al. 2016). Note that prehistoric humans had occasionally employed (and processed) iron oxides that were formed by aquatic, iron oxide-producing bacteria such as *Leptothrix ochracea* (MacDonald et al. 2019; Garilli et al. 2020).

A basic processing of natural ochres includes grinding and washing and, possibly, differential settling, or another size-based separation method, for the generation of grades characterized by a different mean particle size. Quite often the natural candidate (for pigment use) materials were simply hand-picked from surface deposits, yet procurement of ochres through subterranean/underground mining was also often employed since the dawn of prehistory

(Sajó et al. 2015). However, the spotting of ready-to-use ochre deposits is a very rare occasion, and in most of the cases, raw ochres must be processed prior to their use. The degree of processing varies according to the raw material; for instance, high-grade iron oxides can be converted to satisfactory pigments through mere grinding and sieving (Gettens and Stout 1966). Nevertheless, ochre processing often involves three distinct steps, namely (a) removal of large impurities by hand-picking, (b) grinding (occasionally accompanied by sieving), and (c) washing and/or floatation/levigation (Helwig 2007; Siddall 2018). Various ochres were often intermixed in order to produce a pigment of a specific color, while there are strong indications suggesting that the addition of various minerals in natural ochres was practiced since Paleolithic times (Helwig 2007). Moreover, ochre heat treatment for color manipulation is another rather common practice employed since early times (see "Artificial ochres"). Note that both the mixing and thermal treatment of ochres are preferentially practiced after the completion of the (a) to (c) steps.

Through handpicking one may eliminate the large impurity/gangue particles such as quartz or calcium carbonate pebbles and other non-coloring mineral/rock substances, along with roots, leaves, etc.; such a process leads inevitably to an enrichment of the ochreous substances and a color enhancement. The grinding that follows is an essential step as it allows for the manipulation of the pigment consistency through the reduction of the pigment grain size and alteration of grain morphology. Quite often, prehistoric craftsmen simply rubbed-off ochre lumps on the surface to receive decoration (Rifkin 2012; Hodgskiss and Wadley 2017), yet grinding implements such as mortars and pestles along with mullers and slabs made of alabaster and other stones or glass are continuously (and widely) used since antiquity (Gettens and Stout 1966; Mayer 1991; Rosso et al. 2016). Although grain size affects considerably the color, hiding power, and tinting strength of many pigments (see "Mineralogy"), it has been shown that the red and yellow ochres are not affected considerably by grinding (Gueli et al. 2017), most probably because the Fe components that impart color to them are already (i.e., before ochre processing) in the form of very fine particles (Eastaugh et al. 2008). Nevertheless some clues indicate that ochres produced from the same raw materials, yet through different grinding methods, might indeed be of slightly different shades (Rifkin 2012).

Fig. 3 Left: lump of raw yellow ochre from Ymittos Mountain, Attika, Greece. Right: elemental compositions (EDX, wt%, normalized to 100%) and corresponding standard deviations (std) of the several EDX analyses conducted on lumps of the raw and processed (: washed) Ymittos yellow ochre. Sample collection, treatment, and EDX analyses conducted by the authors

	Yellow ochre from Ymittos			
	Raw		Processed	
	wt%	std	wt%	std
Na	0.2	±0.3	0.5	±0.1
Mg	0.1	±0.2	2.0	±0.2
Al	0.7	±0.0	11.5	±1.3
Si	14.8	±9.6	49.4	±1.4
S	n.d.		0.2	±0.2
Cl	n.d.		0.2	±0.3
K	n.d.		3.1	±0.1
Ca	69.9	±9.5	12.5	±0.7
Ti	n.d.		0.7	±0.0
Mn	1.2	±0.4	0.3	±0.3
Fe	13.1	±1.4	19.7	±1.2

Washing and floatation lead to the removal of various hard/heavy accompanying minerals, improving thus not only the grinding properties of the pigment, but its color as well (Helwig 2007). Upon suspension of a mixture in water, its various components will settle down with different sedimentation rates. The latter depend on specific gravity and grain size; therefore, the grains that are coarse and/or of high specific gravity will settle first. For instance, many ochres bear considerable quantities of rather coarse silica and calcium carbonate inclusions that are easily separated upon water suspension; such a partition will lead to substantial reduction of the Si and Ca contents. However, this is not always the case, and a relevant example is presented in Fig. 3, where a yellow ochre lump collected by the authors from Ymittos (Hymettus) Mountain, Greece, is shown. The raw Ymittos yellow ochre was first ground in an agate mortar and pestle and subsequently subjected to successive washings with water. The washing affected considerably the elemental composition of the ochre (estimated via EDX[3]), as the processed (: washed) ochre shows significantly more Al, Si, Fe, and Mg, yet less Ca in comparison to the raw material. This indicates that a calcareous phase (presumably calcium carbonate) was largely removed upon washing, leading thus to an indirect enrichment in clay and iron.

The processing of natural ochres by the methods described above is a rather simple and technically not demanding task; therefore, it was often practiced by the craftsmen themselves up at least the nineteenth century (Helwig 2007). Nevertheless, one notes the scarcity of relevant recipes in the medieval and post-medieval technical literature, and this probably indicates that these processes were considered common knowledge by craftsmen (Thompson 1956).

[3] In order to highlight various aspects related to ochres, authors have occasionally incorporated results deriving from their own research. This is the case of the SEM–EDX analyses/images presented in Figs. 3, 5, 6, 8, 9, and 11, the μ-Raman spectra shown in Fig. 10, and the XRF data shown in Fig. 7. The relevant methodological details are provided in Appendix 2.

Artificial ochres

Manufacturing processes for ochres might rely on chemical changes or on structural changes (restructuring that includes crystallization) or on physical–chemical changes (e.g., sorption of certain species or change of particle size upon coarsening). We will not consider here modifications that result from refinement processes only; we will also exclude manufactured pigments that resemble ochres as regards appearance but exhibit radically different compositions (organic or others).

The pertinent practices can be grouped according to the precursors used, namely those that lead to the production of artificial ochres using (a) earthy ochre-type precursors and (b) high-iron precursors.

Manipulation of natural ochres

Theophrastus describes in detail (DL, 53–54) the accidental discovery of Cydias that a red ochre can be generated upon roasting a yellow ochre, while some fine-tuning of the hue can be achieved through the control of the "intensity" (duration and temperature) of firing (Fig. 4, left). If the Cydias of Theophrastus is the same as the Cydias in Pliny (NH, XXX, 130), then the time of the latter discovery is possibly the mid-fourth century BC; yet various technological aspects of conversion of yellow ochres to brown and red ones were apparently already known during the Bronze Age, while application of the basic idea is possible even in the case of Paleolithic rock paintings (Helwig 1997; Pomiés et al. 1999; Cornell and Schwertmann 2003). Besides, the thermal treatment of ochres is regarded by some scholars as the earliest form of pyrotechnology (Siddall 2018).

Vitruvius (DA, VII.11; see also Pliny NH XXXIII.113) describes a less elaborate firing process than that in Theophrastus but adds a quenching in vinegar step that is claimed to have a substantial effect on hue as the outcome is of a "purpureo colore"; however, some modern replication

Fig. 4 Left: "French ochre", Kremer Pigments (product code: 40010), before (left, major components identified by XRD: goethite, quartz, kaolin) and after firing at 920℃ (right, XRD: hematite, quartz). Right: artificial iron oxy hydroxide prepared by the vinegar route (insert figure) before (left, XRD: goethite) and after firing at 920℃ (right, XRD: hematite). Both figures derive from authors' experimental work

experiments have shown that the vinegar quenching may (at least in some cases) not affect the color of the pigment (Mastrotheodoros et al. 2010). The recipes for ochre thermal treatment persisted well into medieval texts (such as the Strasburg MS and the "De Diversis Artibus") and in many post-medieval painting treatises (Dionysios 1996; Helwig 2007), while according to Harley (1982), the oldest relevant English patent was issued during the seventeenth century (production of red and brown pigments through ochre burning).

In fact, the main change as a result of firing is the formation of a new phase (an oxyhydroxide converts to oxide upon dehydration) (Balek and Šubrt 1995; Pomiés et al. 1999); conversion starts at temperatures in the range of 250–280 ℃, but then the outcome is the so-called "disordered (i.e., purely crystalline) hematite," while a minimum temperature of 850–900 ℃ is necessary for the formation of fully crystalline hematite. In addition, control of the atmosphere is necessary, as black magnetite might also form. Change of particle size (affected by ochre composition, temperature and duration of heating) and presence/removal of impurities are examples of other factors that affect hue. For instance, one may manufacture a deep red/purple hematite pigment by firing an adequate precursor (e.g., goethite) at relatively high temperatures (> 850℃): by this way, hematite particles of enhanced diameter (> 1 μm) and, hence, purple color, are formed (Elias et al. 2006; Mastrotheodoros et al. 2010) (Fig. 4, right).

Finally, it might be of relevance to note the ingenious thermal treatments of ochres that were practiced during antiquity in the manufacturing of black-gloss pottery (Noll et al. 1975; Maniatis et al. 1993; Mastrotheodoros et al. 2013; Aloupi 2020) (Fig. 5).

Employment of high-iron precursors—Mars pigments

The oldest pertinent practices can be traced back in ancient Greek literature: Dioscorides states that (ground) magnetite was converted, upon proper firing, to hematite (E.126, E. 130) and that this was a frequent practice. The magnetite to hematite (the coloring constituent of miltos) conversion

Fig. 5 **a** Vitrified black gloss layer on top of a ceramic body; archaic pottery sample (Greece, sixth century BCE), SEM image, magnification 1,700×. **b** Black gloss decoration, partially covered by deep red hematite; Corinthian pottery sample (Greece, sixth century BCE), stereoscope, 10×. **c** Detail of the hematite particles that color the deep red decoration shown in (**b**); SEM, 138,621×. Authors' archive

is due to Fe(II)→Fe(III) oxidation which takes place in oxidative atmospheres from a temperature of about 350 to 400 °C (while at about 250 °C maghemite might form) (Przepiera and Przepiera 2001; Cornell and Schwertmann 2003). Mineral hematite was also occasionally grinded in order to produce a red pigment, yet this practice is documented in the much later "Il libro dell' arte" (circa 1400 CE), where the specific pigment is called "amatisto" and considered as distinct from red ochre and particularly suitable for fresco painting (Broecke 2015). However, one may note that the pure hematite mineral is less available than natural red ochres and that hematite mineral is difficult to grind; as Cennini notes, "amatito" pounded on a porphyry slab might crack it ("Il libro dell' arte", chapter 42, see Broecke 2015).

New ochre fabrication approaches that employed other iron-rich precursors developed gradually, already from Hellenistic times, in part as a result of alchemical activity; when, eventually (say at the time of the death of Isaac Newton), alchemy faded, fabrication processes become more standard, and manufactured ochre products became widely available. In principle, the production of yellow ochres should employ a solution method (that will allow for the incorporation of hydroxyls to the product), while the fabrication of a red ochre might rely largely on firing (that might lead to oxidation, to dehydration, or to decomposition of the precursor material), while a solution step precedes in some cases.

Various routes leading to the production of yellow ochres are described in detail by Buxbaum and Pfaff (2005) and Schwertmann and Cornell (2000); in principle, high-quality synthetic yellow ochres can be more difficult to prepare than corresponding red ochre pigments (Leskelä and Leskelä 1984). On the other hand, brown and purple ochres can be prepared more easily upon involvement of manganese in yellow and red ochre recipes, while mere ochre darkening can be also achieved via mixing with carbon black. As regards manganese involvement, this is possible either through preparation of single-phase products (with both iron and manganese cations) or through mechanical mixing of an iron-containing phase and a manganese-containing phase, the latter being the most common option (Buxbaum and Pfaff 2005).

Given the fact that during antiquity lead and copper were exposed to vinegar in order to form the popular lead white and copper green pigments respectively, it is possible that a version of the same technique was occasionally used for the generation of ochres from iron metal. An experimental exploration of this possibility showed that it may lead to the production of pure goethite which can be further treated thermally in order to manufacture hematite with various particle sizes (Mastrotheodoros et al. 2010). As the hematite grain size can be manipulated by adjusting the firing temperature (op. cit., Gialanella et al. 2010), pigments that cover the range between brown yellow (red) to purple can be produced (Fig. 4, right).

Besides, some red ochres were indeed fabricated via simple methods, such as firing of ferrous sulfate or other iron salts, roasting of iron/steel fillings, and dissolution of iron fillings in a strong acid, followed by drying and calcination (Harley 1982). Presumably some of these methods emerged in the frame of antiquity medicinal practices, and there exist some pertinent Indian recipes that date back to the Ayurvedic period (~ 600 BCE–800 CE) (Helwig 2007). In addition, European medieval alchemical and other texts bear descriptions of artificial iron oxide (or hydroxide) production through, e.g., calcination of iron sulfate ("green vitriol") (Theophilus 1979, Book III, chapter 40). It appears that at least some of these manufactured materials had been occasionally used as painting materials from as early as the sixteenth century (Helwig 2007).

Nevertheless, it was not until the end of the eighteenth century that the manufactured iron pigments became widely available. During that times (and in the frame of the industrialization), new, more efficient methods of iron oxides (/ hydroxides) production emerged, leading to the production of the so-called "Mars pigments" (yellow, orange, red, brown, and violet) (Harley 1982; Helwig 2007; Eastaugh et al. 2008). Pertinent names derive ultimately from alchemical names, e.g., "Mars yellow" derives from "crocus martis" (Harley 1982); the reference to Mars, the god of war, reflects the employment of iron, the metal of weapons.

For the manufacturing of a "Mars yellow," one might add alum to a solution of ferrous sulfate, induce precipitation with alkali addition (e.g., lime or potash), and eventually obtain the desired product upon air exposure of the precipitant (Harley 1982). The proportion of alum affects the tonality of the yellow pigment (Gettens and Stout 1966), while in the absence of alum addition, the formation of yellow ochre with a brownish hue is possible. Subsequent firing and/or additional ions (of manganese and other metals) and other substances lead to additional (brown, orange, red, crimson, violet) Mars pigments.

The decomposition or decomposition + oxidation approach can also be applied to other Fe(II) and Fe(III) salts, such as iron chloride, iron nitrate, and iron acetate (Eastaugh et al. 2008; Nicola et al. 2016), while in the frame of current practices, additional starting materials are being employed such as mill-scale iron wastes that lead to a sustainable and cost-efficient pigment production (Sikalidis et al. 2006; Legodi and de Waal 2007). Hence, current artificial ochre pigments exhibit a typical purity of at least 95%; nevertheless, if the target is a material exhibiting a broad spectrum of characteristics similar to those of natural ochres, other phases of substantial extent might be intentionally included. Besides, Mars pigments may indeed be mixed mechanically with native clay-rich materials (Hradil et al. 2003), while Gettens and Stout (1966) mention that occasionally the Mars pigments are sold for the natural ochres.

However, some of the reagents that are used in the production of Mars pigments may either react only partially, or (/and) form new soluble salts. This means that the corresponding products may contain unwanted substances, which must be removed through washing prior to any further pigment processing (Gettens and Stout 1966). Besides, there are certain cases in which soluble salts are detected even in the final (presumably washed) product (Franquelo and Perez-Rodriguez 2016). Further processing of Mars pigments may include the addition of other substances such as native clay-rich material, gypsum, barite, aluminum oxides, and/or other pigments (Hradil et al. 2003; Nicola et al. 2016), in purpose of adjusting optical and working properties.

On the other hand, contemporary production processes are well-controlled and lead to pigments of pre-defined particle size characteristics (mean size, size distribution, and shape) (Buxbaum and Pfaff 2005), while various waste materials are currently given consideration as potential pigment precursors (see, e.g., Legodi and de Waal 2007; Fiuza et al. 2018). However, the first industrial-scale production processes were of relatively low yield; therefore, the early Mars pigments were rather expensive, and the older relevant practices (e.g., calcination of iron sulfate and yellow ochre) persisted well into the nineteenth century (Helwig 2007).

Finally it is noteworthy that the term "Mars pigments" is sometimes used for all artificial pigments based on Fe(III) oxides and hydroxides. However, various modified and fully synthetic yellows, reds, browns, etc. based largely on Fe(III) oxide[s] and hydroxides are/were known with different names; examples are the Persian, Indian, and Venetian reds, which replaced natural reds with the same names (Eastaugh et al. 2008).

The application of ochres

Iron oxide pigments are very stable: they are lightfast, inert in mixtures with other pigments, and stable to dilute acids and alkalis, and they do not react with the common binders and organic solvents that are employed in painting (Helwig 2007; Coccato et al. 2017). Moreover, they have rather high refractive indexes (often > 2.00), and, hence, they are of excellent hiding power; on the other hand, their tinting strength depends largely on particle size (Helwig 2007).

Ochres have been widely employed in various kinds of painting such as tempera and oil (Gettens & Stout 1966; Mayer 1991). Besides, due to their resistibility against alkalis, ochres have been extensively employed in fresco painting as well, where the alkaline conditions induced by calcium hydroxide hinder the employment of certain other vulnerable pigments (Dionysios 1996; Helwig 2007; Broecke 2015). It is worth mentioning that back in 1956, the renowned scholar of medieval painting D. V. Thompson (1956) supported that ochres were not employed in miniature painting (due to their low color intensity); nevertheless, recent analytical investigations have shown that ochres were occasionally used for manuscript illumination as well (e.g., Aceto et al. 2012).

Interactions, stability, and compatibility

Iron oxide/hydroxide pigments are generally deemed as stable compounds; hence, they have been employed in painting with all the available binders, such as proteinaceous substances, gums, siccative oils, wax, lime water, and synthetic polymers. Nevertheless, iron oxide pigments may undergo alteration under specific conditions. For instance, goethite and lepidocrocite are readily transformed to hematite upon heating in moderate temperatures (> 120℃) due to the loss of physically and structurally bound water (Balek and Šubrt 1995; Walter et al. 2001; Buxbaum and Pfaff 2005). Maghemite and magnetite may also form during hematite heating: maghemite is formed upon firing in presence of organics, while firing at higher temperature and/or at reducing atmosphere favors the formation of magnetite (Helwig 2007). The Pompeian frescoes represent the most famous instance of accidental thermal conversion of yellow iron pigments to red ones (Nicola et al. 2016); the reverse process (hydration of iron oxides) may also occur, yet such cases are rather rarely documented in the literature (Nicola, op. cit.).

On the other hand, Church (1915) mentions that yellow ochre in all media (and especially in oil) eventually becomes somewhat darker and warmer in hue and that the ochers might also affect some lakes, as the iron(III) of the former might replace some of the aluminum of the alumina support of the latter. Indeed, recent studies have shown hematite reducing the thermal stability of rabbit skin glue (Ghezzi et al. 2015), as well as that it inhibits oxidative polymerization and promotes chain scission processes in oil mediums; therefore, oil paint layers that contain relevant pigments are rather sensitive to solvents (Helwig 2007). Besides, Poli et al. (2017) also suggest that the ochres may slow down photo-oxidative processes. On the contrary, manganese accelerates the drying of oils; hence, umbers were sometimes recommended as siccatives in painting treatises (Helwig 2007, see also the Turquet de Mayerne manuscript/British Library, Sloane MS 2052), while recent studies have shown that both manganese and iron oxide contribute to the degradation of fats (Bernardino et al. 2014; Horn 2018).

Adulteration and competitors

Ochres are stable and neither poisonous nor interacting with most pigments (Helwig 2007; Coccato et al. 2017), and, hence, some of the usual reasons for pigment displacement are not applicable to ochers. In addition, ochers are abundant; therefore, they might not be expensive materials (Harley 1982, Hradil et al. 2003). Nevertheless, natural ochres of substantially different quality and price always existed, while the brightening of the natural, somewhat dull color of ochres might have been often desired in the frame of pigments' trade. Consequently, attempts to produce more attractive or lower-priced products are unavoidable, and adulteration, imitations, etc. existed already from antiquity or even prehistoric times (Helwig 2007). Whitish earths, calcium carbonate, and fine quartz powder are some possible additives that will favor lighter ochre hues (David et al. 2001). A list of practical tests for the assessment of the "genuineness" of yellow ochre pigments found in Doerner (1984) suggests the wide circulation of ochres adulterated with organic and other components at the time of Doerner's work, originally published in 1933. Besides, additions of organics (both natural and synthetic ones) to natural ochres might create or intensify desirable hues but the result will be much less permanent than that achievable by ochres alone. On the other hand, early artificial iron oxide pigments often contained residues of the starting materials (e.g., ferrous sulfate) that might have had a negative effect on certain organic pigments or other substances (Helwig 2007).

Today that the palettes of the painters are usually dominated by paints based on organics, one also encounters advertisement of ochre-based artistic paints modified via the addition of organic pigments for the boosting of the ochre color, or for the imitation of the hues of certain exhausted or nearly exhausted and/or expensive ochres, siennas, and umbers. Some other combinations are recognizable as separate materials, such as the, already discussed, syricum of the Greco-Roman times and the "golden ochre" (yellow ochre brightened with chrome yellow) that circulated around the beginning of the twentieth century (Eastaugh et al. 2008).

Nowadays natural ochre pigments have been largely displaced by synthetic ochres (based on Fe(III) oxides and hydroxyoxides), in which case availability and fixed product features (e.g., composition and grain size) can be guaranteed. Chemically speaking, processes that lead to the formation of goethite, hematite, etc. from other iron sources (e.g., via oxidation of iron fillings, see Employment of high-iron precursors—Mars pigments) generate new "true" ochres and not imitations. Additional phases similar to those included in natural ochres (e.g., clay materials) might be added to synthetic ochres in purpose of manipulating pigment properties (Hradil et al. 2003), while Mars pigments might occasionally be sold for the natural ochres (Gettens and Stout 1966).

As for the red ochre competitors, the key red pigments of antiquity were those based on cinnabar and minium (Katsaros and Bassiakos 2002; Gliozzo and Ionescu 2021; Gliozzo 2021), while realgar (e.g., Dioscorides E.122, Strabo 12.562) was a less frequently used pigment. On the other hand, apart of yellow ochres (including jarosites), the key yellow mineral pigment of antiquity was orpiment (e.g., Vitruvius VII.7, see FitzHugh 1997; Gliozzo and Burgio 2021), while massicot (PbO; mostly artificial, rarely volcanic natural) was of some use during the Middle Ages and possibly during antiquity as well (FitzHugh 1986); as far as we know, anything else (e.g., wulfenite ($PbMoO_4$) in Ur, see Bimson 1980) was only rarely used. The next important yellows in painting were lead stannate (from fourteenth century AD in Europe) and lead antimonate (mostly (?) from seventeenth century AD in Europe, see Agresti et al. 2016); the latter though was employed as a glass and glaze colorant already during the second half of the 2nd millennium BC. Organics in the form lakes were less permanent competitors of red and yellow ochres, while the pigment Indian yellow appeared in Europe during the fifteenth century AD (Eastaugh et al. 2008; Ploeger and Shugar 2017).

Ochres in painting and gilding substrates

Ochres have found wide application as priming/ground materials for painting. During the middle ages, wooden panels were routinely receiving preparatory (ground) layers that were made of gypsum or chalk mixed with organic glue (Thompson 1956). Nevertheless, since at least the fifteenth century, western European craftsmen started adding colored compounds in their ground mixtures, and from the sixteenth onwards, ochres were customarily used as priming materials (either alone or mixed with chalk, gypsum, or other materials) (Duval 1992; Hradil et al. 2003; Helwig 2007; Stols-Wiltox et al. 2012). In fact, the presence of a colored substrate (: ground) may affect considerably the tonality/hue of the superficial paint layers, while in some cases, the colored grounds themselves have been left intentionally uncovered by the painters to serve as part of the composition (Grygar et al. 2003; Stols-Wiltox et al. 2012). It is interesting to note that although the Greek religious icon painters remained adhered to the use of traditional gypsum grounds throughout the post-Byzantine period (1453 to 1830 AD), the addition of minor quantities of ochres in Greek icons' grounds is occasionally documented as well (Milanou et al. 2008; Mastrotheodoros et al. 2016).

On the other hand, red and yellow iron earths were customarily employed as substrates for water gilding from the middle ages onwards (Thompson 1956; Mactaggart and Mactaggart 2002). Quite often the relevant earths were called "boles," and vice versa, the term "bole" was sometimes used as a synonym for "red ochre" (Harley 1982; Eastaugh et al. 2008). However, in most of the cases, "bole"

pertains to a special type of iron-rich fine clay "of velvety smoothness" that is used in the frame of gilding and/or for the production of colored grounds (Grygar et al. 2003). Sometimes the term is loosely defined as it may include any earthy substance that is used as a gilding substrate/poliment, regardless of its color (e.g., gray bole, green bole) (Mactaggart and Mactaggart 2002), while mixtures of various materials including clay minerals, chalk, and gypsum were occasionally labelled "boles" and used as gilding substrates (Hradil et al. 2017). One of the most famous relevant earths, the so-called Armenian bole, was used as a medicinal since antiquity and as a poliment since at least the eleventh century AD (Hradil et al. 2017). Nevertheless, the adjective "Armenian" was often used as a means to denote a bole with specific quality/properties rather than origin (Hradil et al. 2003; Barata et al. 2015), and it seems that the circulation of genuine Armenian bole had already ceased in Europe during the sixteenth century (Helwig 2007).

The earths that are used as gilding substrates/boles may differ substantially from the ochres employed for pigmenting purposes. This is evident in Fig. 6, where the elemental compositions (Fe vs Al + Si) of ochres and boles from tenths of Greek post-Byzantine (mid-fifteenth to early nineteenth century) icons are plotted: the boles are of a moderate to low iron content and significantly richer in aluminosilicates in comparison to ochres. However, there is a small overlapping of boles and ochres compositions, and this is reminiscent of the "Hermeneia" text (Dionysios 1996) where the boles that are used as poliment ingredients are occasionally recommended as painting (: pigment) materials as well.

Finally, we shall make a short comment regarding the presumable effect of the bole color onto the gold leaf appearance, which is shared among many contemporary craftsmen. Although older analytical investigations were in favor of this hypothesis (e.g., Mounier and Daniel 2013; Barata et al. 2015), recently published studies suggest that the effect

of the substrate on the color of the leaf is in fact too faint to be perceived by the human eye (Wu et al. 2020a, 2020b).

Analytical investigation of ochres

Phase identification, elemental composition, and micro-morphology (i.e., grain/particle size and shape) are the most important aspects explored in the frame of ochres' analytical investigation. The relevant analytical techniques include the widely employed X-ray diffractometry (XRD), spectroscopic techniques such as Fourier Transform Infrared (FTIR), Raman, Mössbauer and ultraviolet–visible (UV–Vis) spectroscopy, optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), thermal analysis techniques (thermogravimetric analysis-TGA, differential thermal analysis-DTA and differential scanning calorimetry-DSC), magnetometry, chemical testing etc. (Cornell and Schwertmann 2003; Helwig 2007). Other techniques have been occasionally employed as well, such as neutron activation analysis (NAA) (Popelka-Filcoff et al. 2007; MacDonald et al. 2011), iron isotope analysis (Eerkens et al. 2014), voltammetric analysis (Grygar et al. 2002; Hradil et al. 2003), along with solution, and laser ablation inductively coupled plasma-mass spectrometry (ICP-MS & LA-ICP-MS, respectively) (Bu et al. 2013). As an in-depth coverage of this topic is out of the scopes of the current work, we will present and comment on selected analytical techniques providing bibliographic references for further study. For reasons of convenience, the material in consideration is arranged in three major subsections, namely "X-ray diffraction," "Spectroscopic techniques," and "Microscopic techniques"; special subsections are devoted to the "Provenancing ochres" and to a brief summary of "Good practice" guidelines.

X-ray diffraction

X-ray diffraction (XRD) is regarded the commonest and most reliable technique for the identification of the crystalline iron oxide/oxyhydroxide and clayey components of ochres (Cornell and Schwertmann 2003; Hradil et al. 2003). X-rays are scattered by the lattice atoms of crystalline matter in a way that is characteristic of the lattice parameters themselves; therefore, XRD yields information that pertain to the crystal structure of the analyte. The principles and possible applications of the method are described in detail elsewhere (Waseda et al. 2011; Zolotoyabko 2014).

Conventional XRD often requires a substantial amount of sample (usually 1–2 g), and this might be a problem in case of artworks/archaeological items analysis; indeed, quite often there is limited access to the relevant objects,
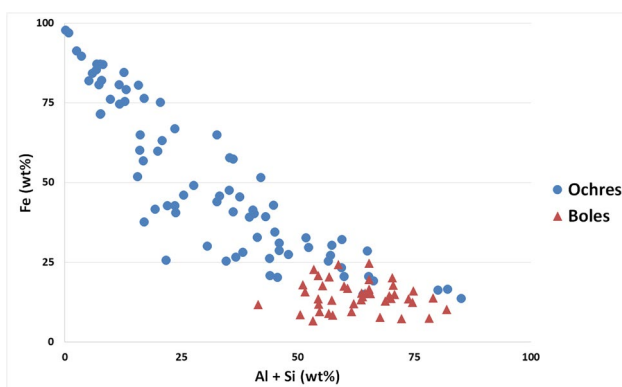
Fig. 6 Fe versus Al plus Si contents (wt%, EDX) of ochres (circle) and gilding boles (triangle); samples from Greek post-Byzantine icons (authors' data)

and, hence, collection of substantial samples is impossible. However, one may overcome this problem through the employment of micro-diffraction (μ-XRD) and synchrotron radiation diffraction (SR-XRD) techniques that allow for the analysis of minute samples and give back diffractograms of improved statistics, making possible the analysis of samples that bear low concentrations of crystalline compounds (Herrera et al. 2008, Švarcová et al. 2008). This possibility is extremely useful when it comes to the investigation of samples' cross-sections (either thick or thin), as one may collect diffractograms from single pigment grains (Romero-Pastor et al. 2011; Pouyet et al. 2015). On the other hand, these techniques employ laboratory equipment, and this is indeed a drawback when it comes to field work. However, high-precision portable XRD devices are currently becoming available, allowing thus for the in situ, conventional XRD investigation of artifacts (Hirayama et al. 2018).

Each crystalline compound has its own characteristic diffraction pattern that leads to definite identification; charts of diffraction data are accessible in the pertinent literature (Cornell and Schwertmann 2003; Helwig 2007) and in several online databases (see for instance ICDD and rruff). Conventional, micro, and synchrotron radiation XRD analysis is employed in numerous studies pertaining to natural and artificial ochres (e.g., Montagner et al. 2013; Moyo et al. 2016; Garofano et al. 2016; Dimuccio et al. 2017). Interestingly, studies have shown that the diffraction pattern of disordered hematite (or proto-hematite) is differentiated from that of fully crystalline hematite due to a characteristic broadening of some reflections. As disordered hematite is formed upon firing of goethite at relatively low temperature ($< 600°C$), the spotting of samples with the pertinent diffraction pattern has led to the identification of artificial (i.e., produced through goethite thermal treatment) hematite in several instances (Helwig 1997; Pomiés et al. 1999; Cavallo et al. 2018). Note, however, that variations in diffraction patterns may also arise due to partial iron substitution in the crystal lattice and changes in a compound's particle size and shape, while low crystallinity or absence of crystallinity may even preclude identification through diffraction techniques (Helwig 2007; Cloutis et al. 2016). In the latter case (low crystalline or amorphous compounds), spectroscopic techniques such as Raman and FTIR offer good chances for certain identification.

Spectroscopic techniques

Spectroscopy explores the interaction of radiation with matter; the type of interaction (e.g., electronic orbital transitions or changes in the molecular vibration modes) depends on the energy (: wavelength) of the radiation and the elemental composition or (/and) molecular structure of the analyte. Of the various spectroscopic techniques that are nowadays available, authors picked out and present below X-ray, Raman, infrared, and UV–Vis spectroscopies, along with a couple of less frequently used ones.

X-ray spectroscopy

X-ray fluorescence is generated via the interaction of high energy photons, electrons, or protons with matter, a phenomenon exploited in the frame of various analytical techniques such as X-ray fluorescence (energy or wavelength dispersive ED/WD-XRF), X-ray spectroscopy coupled with scanning electron microscopy (SEM–EDS/WDS), and proton/particle induced X-ray emission (PIXE). In all these cases, the excitation beams that interact with the targets expel inner shell electrons causing thus the emission of characteristic X-rays; the latter are collected and plotted on energy intensity x–y plots (spectrum) yielding thus information pertaining to the elemental composition of the analyzed matter (Van Grieken and Markowicz 2002; Janssens 2004; Beckhoff et al. 2006).

XRF is probably one of the most widely applied spectroscopic techniques in the field of archaeometry; besides, recent advances in X-ray sources and detectors have led to the wide dissemination of portable devices (p-XRF) that are routinely employed in the investigation of artifacts and archaeological items, as well as in the analysis of mineral industrial materials, etc. Also, improved optical systems allow the focusing of the X-ray beam down to less than 100 microns, while the employment of synchrotron radiation (SR) leads to a spatial resolution in the level of one micron (e.g., Paternoster et al. 2005; Janssens and Cotte 2020).

However, in case of conventional XRF, one may face certain limitations[4] as regards the analysis of light elements ($Z < 12$, Mg) which are of importance when analyzing pigments. Nevertheless, XRF has a good excitation efficiency for heavier elements including iron (the characteristic ochre element); hence, it allows for a rapid screening of samples that may often lead to a first classification of pigments and eventually to the identification of important fingerprinting characteristics (Popelka-Filcoff et al. 2007; Hodgskiss and Wadley 2017, Dimuccio et al. 2017). Moreover, the recently emerged macroscopic XRF setups (MA-XRF) allow for the two-dimensional scanning of artifacts and the generation of elemental distribution maps (Romano et al. 2017). Therefore, it is possible to assess the spatial distribution of pigments on artifacts/paintings through screening for characteristic elements. A graphic example is provided in Fig. 7a that shows the spatial distribution of iron on a detail of a nineteenth century miniature Slavic icon (Fig. 7b).[5] This particular elemental distribution map highlights the employment of

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[4] In fact the low energy photons are absorbed by atmospheric air. A way out of this problem is the target excitation in vacuum or in helium flow.
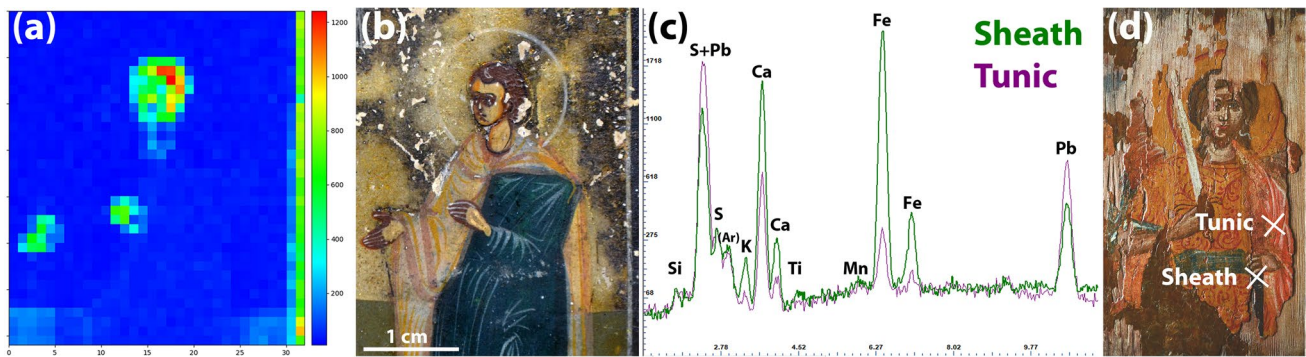[5] Experimental details are provided in Appendix 2.

Fig. 7 **a** and **b** Fe elemental distribution map (**a**) and detail of a nineteenth century Slavic miniature icon (**b**). **c** and **d** XRF spectra (**c**) collected from the sheath and the tunic of a Greek post-Byzantine (eighteenth century) icon (**d**). Data by the authors

ochres only on the flesh parts, the hair, and the borderline, while the lower level of iron detected in the green ground presumably reflects the employment of a Prussian blue (Fe) + chromate yellow (due to Cr detection) mixture. By such an approach, scholars are often able to scan the whole surface of paintings, revealing thus important information regarding artists' original palletes and latter interventions.

However, it is important to keep in mind that the highly energetic X-ray photons are able to penetrate relatively deep (several tenths of microns) into matter; the penetration depth depends on both the X-ray beam energy and the absorption coefficients of the analyte components (Van Grieken and Markowicz 2002). Therefore, when analyzing multi-layer structured materials such as paintings, the collected photons may well originate from multiple layers. For this reason, pertinent XRF data should be critically assessed in order to avoid misconceptions. A relevant example is shown in Fig. 7c that depicts two spectra collected[6] from a late eighteenth century Greek icon: the spectrum from Archangel's sheath (painted in brown ochre) shows Pb spectral lines, which originate from the orange-red tunic that lays beneath and was rendered in minium. By simply evaluating the first spectrum, one might have reached to the erroneous conclusion that the sheath was rendered in an ochre plus a lead-based pigment mixture.

On the contrary, being particles, the electrons that are employed in SEM–EDS/EDX analysis often penetrate far less than a micron into matter (Egerton 2005); thus, interference phenomena related to sublayers are improbable in case of paintings, where paint layers often measure tenths of microns in thickness. In fact SEM–EDS analysis is routinely employed for the determination of the elemental composition of minerals, bulk pigments and pigment grains in samples' cross-sections (e.g., Chalmin et al. 2003;

Genestar and Pons 2005; Aliatis et al. 2010; Gliozzo et al. 2012; Franquelo and Perez-Rodriguez 2016; Dayet et al. 2019; Mastrotheodoros et al. 2021). The major advantage of SEM–EDS over XRF is the capability of detecting light elements (with $Z \geq 6$, C) along with the possibility of acquiring high-quality and high magnification photomicrographs (see "Microscopic techniques"). However, SEM–EDS is often regarded as a micro-destructive technique because the relevant devices can only accommodate specimens of rather limited dimensions, and, hence, sampling is often required. In addition, prior to examination with conventional SEM devices that operate in the high-vacuum mode, samples need to receive treatment(s) that lead to (usually severe) alterations. Nevertheless, the latter issue can be overcome through the employment of environmental SEM devices (ESEM) that allow for the investigation of samples in the as-received state (no pre-treatment needed).

Quite often, the SEM–EDS data that pertain to ochres' elemental composition derive from paintings' investigations. Within this framework, scholars usually determine the elemental compositions of paint layer(s), rather than individual pigment grains (see for instance Hein et al. 2009; Marić-Stojanović et al. 2018). Nevertheless, paint layers may often contain multiple pigments and non-pigment admixtures; therefore, the acquired elemental composition may deviate substantially from that of a given pigment. A relevant example is shown in Fig. 8, where the SEM–EDS analyses of a yellow-colored sample cross-section are depicted.[7] The SEM–EDS spectrum from the yellow paint layer (Fig. 8c-bottom) shows that calcium prevails over iron, while the SEM–EDS spectrum from an individual yellow grain is Fe-dominated. The particular cross-section originates from the mural paintings of sixteenth century Greek church that was painted in the frame of the post-Byzantine religious painting trend; within this trend, the

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[6] Spectra collected by the authors. For experimental details, see Appendix 2.

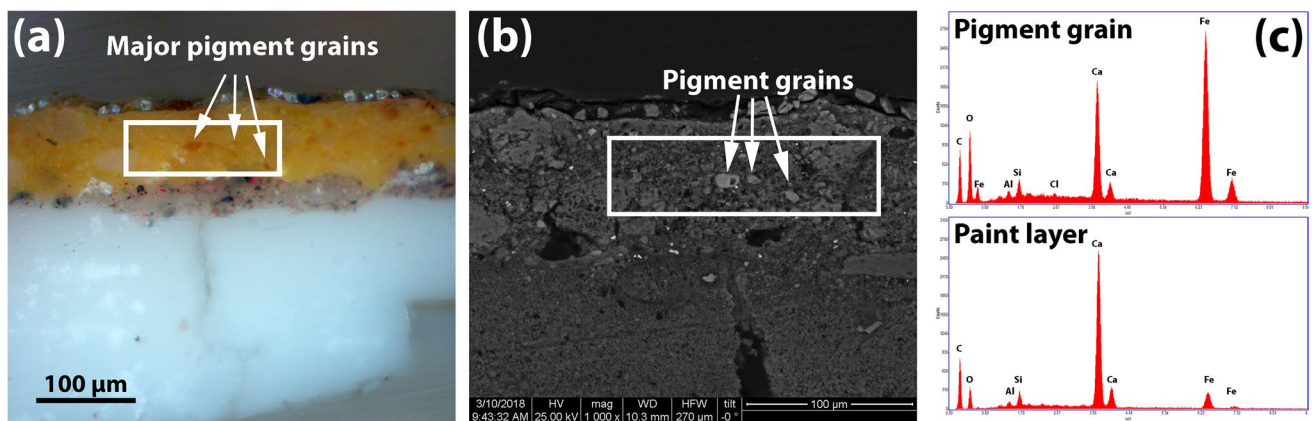[7] Analyses conducted by the authors. The experimental details are provided in Appendix 2.

Fig. 8 a Sample cross-section, OM, 200×; the rectangle marks the analyzed (SEM–EDS) area, and arrows mark on ochre grains. **b** Detail of the analyzed area (rectangle) and individual pigment grains, SEM, 1000×. **c** Bottom: SEM–EDS spectrum collected from the paint layer area marked on (b); up: SEM–EDS spectrum from an individual ochre grain. Data by the authors

pigments were often mixed with lime putty prior to their application on the plaster (Mastrotheodoros et al. 2019).

At this point, we shall make a further comment as regards the determination of natural ochres' elemental compositions by SEM–EDS. Data deriving from multiple pigment grains are mostly presented in the form of mean values in the relevant literature (e.g., Ajò et al. 2004; Genestar and Pons 2005; Hein et al. 2009; Demir et al. 2018). Nevertheless, natural ochres almost always consist of mixtures rather than pure minerals; hence, the corresponding pigment grains are of varying compositions. As mean values do not represent ochres' compositional variations, we suggest to plot the SEM–EDS results obtained through the analysis of multiple single grains. An indicative example is offered in Fig. 9: here, we plot the Fe versus Al+Si (wt%) contents of individual
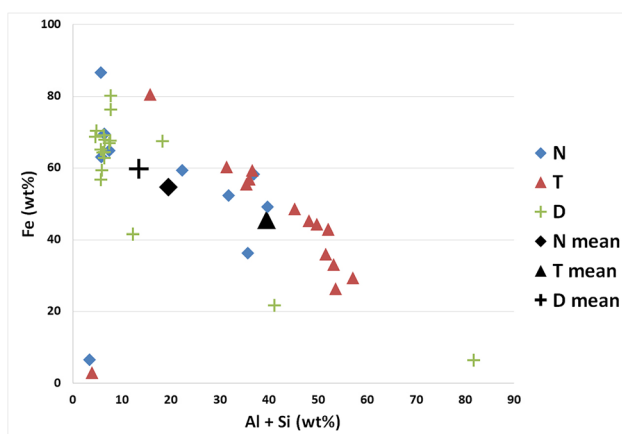
yellow ochre grains that were spotted on wall painting samples originating from three post-Byzantine churches, namely St Nikolaos (N), Transfiguration (T), and St Dimitrios (D). These monuments are located in Epirus, NW Greece, and were painted by the same workshop (Kontaris brothers) during mid-sixteenth century; hence, one might expect employment of the same yellow ochre throughout. The corresponding mean values (black spots—Fig. 9) indicate that the St Nikolaos (◆) and St Demetrios (+) ochres are of very similar elemental profile. Nevertheless, the plotting of the single-grain SEM–EDS analysis results suggests that in fact, the St Demetrios church ochre (+) deviates substantially as it is of a well-defined composition with only few outlying (in terms of composition) grains. This case study highlights that the plotting of single-grain SEM–EDS analyses results allows for a better understanding of the compositional variations of ochres.

Finally, particle-induced X-ray emission spectroscopy (PIXE) is also occasionally employed in the analysis of pigments and relevant materials (Johansson et al. 1995; Calligaro et al. 2004; Lazic et al. 2018). PIXE allows for the elemental characterization of materials and is characterized by its high precision and very low detection limits for certain elements; therefore, it may be used in provenance studies (see "Provenancing ochres") (Beck et al. 2011). Nevertheless, the technique employs highly specialized and mostly immovable equipment; hence, the pertinent facilities are rather rare, and there are only few portable PIXE devices that can be used for the in situ investigation of artifacts (Pappalardo et al. 2003; Romano et al. 2012).

Raman spectroscopy

Raman spectroscopy involves monochromatic light sources (lasers) for the samples' excitation and allows for the determination of the vibrational modes of molecules that relate

Fig. 9 Elemental compositions of yellow ochres from the wall paintings of St Nikolaos (N), Transfiguration (T), and St Dimitrios (D) churches (Epirus, NW Greece). Colored symbols correspond to single-grain EDS analysis results and black ones to the relevant mean values. Data by the authors

to their structure; besides, Raman inelastic scattering takes place when photons induce changes in the vibrational energy of molecules and crystal lattices (Edwards and de Faria 2004; Smith and Clark 2004; Vandenabeele 2013). Raman spectroscopy (especially micro-Raman/μ-Raman) is routinely employed in the field of pigments analysis as it allows for the unambiguous identification of substances through the comparison of the collected spectra with relevant spectra libraries (Bell et al. 1997; Bikiaris et al. 1999; Burgio and Clark 2001; Castro et al. 2005, Froment et al. 2008; Dimuccio et al. 2017; see also various online databases such as RRUFF). Moreover, through the relatively recent employment of confocal optics in μ-Raman spectroscopy, analysis of submicron pigment grains can be achieved (Marcaida et al. 2019). A notable advantage of Raman spectroscopy over XRD is the ability of the former to identify amorphous substances (Franquelo et al. 2009). In Fig. 10-left, a μ-Raman spectrum collected by the authors from a red ochre grain (: hematite) is shown; the corresponding sample originates from mid-sixteenth century Greek wall paintings.

However, attention must be paid on the intensity of the employed laser, as some pigments may undergo severe thermal alteration upon exposure to high-intensity radiation (Bersani et al. 1999; de Faria & Lopes 2007). This is the case of the yellow ochre (: goethite) grain shown in Fig. 10-right, which was thermally altered upon Raman analysis. Moreover, fluorescence phenomena occasionally arise (due to, e.g., the presence of organic binders in painting samples), which may even preclude pigment identification (Castro et al. 2005; Košařová et al. 2013). Finally, it is important to note that the intensity and number of Raman shifts of a given pigment depend on both the excitation laser wavelength and the matrix (organic binding medium in case of painting samples); therefore, notable variations as regards the diagnostic Raman shifts may occasionally occur (Castro et al. 2005; Košařová et al. 2013).

Other spectroscopic techniques

Fourier transform infrared (FTIR) spectroscopy is based on the interaction of infrared radiation with matter. When a substance is irradiated with infrared radiation (wavelength range: 0.7 to 500 μm, i.e., 14,000–20 cm^{-1}) part of the latter may be absorbed due to changes in molecules' movements (through vibrational, rotational, and translational transitions). Molecular vibrations are characteristic to the *structure* of matter; therefore, the corresponding absorptions allow for the characterization and identification of the analyzed compound (Derrick et al. 1999; Cornell and Schwertmann 2003; Edwards and de Faria 2004). Various modes of FTIR spectroscopy such as transmittance, attenuated total reflection (ATR), and diffuse reflectance (DR) have found wide application in the field of pigment identification studies. Besides, iron oxides and hydroxides can be distinguished on the basis of their characteristic infrared absorption bands (Bikiaris et al. 1999; Cornell and Schwertmann 2003), while through the identification of accompanying minerals' functional groups (e.g., hydroxyls, sulfates, and carbonates), it is possible to distinguish different natural ochres (Genestar and Pons 2005). Therefore, the differentiation of ochres on the basis of FTIR identification of iron compounds and accompanying minerals is routinely employed in pigments' studies (e.g., Franquelo et al. 2009; Montagner et al. 2013; Franquelo and Perez-Rodriguez 2016; Moyo et al. 2016; Dimuccio et al. 2017; Manfredi et al. 2017).

Various other spectroscopic techniques that are based on the interaction of ultraviolet, visible, and infrared light with matter have also found application in the identification of ochres (Cornell and Schwertmann 2003; Helwig 2007). Conventional spectrophotometers are capable of recording diffuse reflectance in the UV, visible, and the shortest waves of near infrared light (usually from 200 to 1000 nm), yet during the last decades, portable devices with a sensitivity extending up to 2500 nm have been routinely employed. Besides, pertinent techniques such as FORS (fiber optics reflectance spectroscopy; note that the same abbreviation may also stand for "fiber optics Raman spectroscopy") are totally non-invasive and allow for a rapid identification of pigments; therefore, they have found wide application in the investigation of works of art (Mortimore et al. 2004; Aceto et al. 2012; Cosentino 2014; Garofano et al. 2016). It is

Fig. 10 Left: characteristic Raman shifts of a red ochre grain (hematite); the shift at 660 is presumably due to silicate. Right: goethite Raman spectrum; arrow on the insert microscope caption indicates thermal alteration induced by the excitation laser (514 nm). Data by the authors
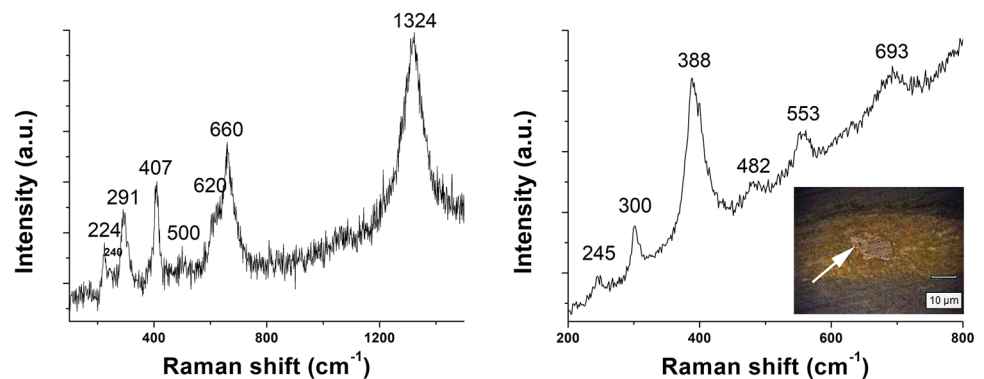
worth mentioning that, although the possibility of identifying clay constituents in ochre pigments is well attested (Corradini et al. 2021), one must pay special attention when analyzing samples of mixed pigments, as in some cases minor mixture components may go unnoticed (Biron et al. 2020).

Mössbauer spectroscopy explores the magnetic behavior of iron in crystal lattices yielding information on iron charge and coordination (Cornell and Schwertmann 2003; Fultz 2011), while certain Mössbauer spectra characteristics pertain to analytes' particle size and cation substitution in crystal lattices (Casellato et al. 2000; Wagner and Kyek 2004; Helwig 2007). This technique has been primarily utilized in the determination of ceramics' firing conditions (Bitossi et al. 2005), but it has been occasionally employed in the identification of raw ochres and painting samples as well (Calvacante et al. 2011; Dubiel et al. 2011; Lehmann et al. 2016, 2017; dos Santos et al. 2018). Although conventional Mössbauer spectroscopy may lead to the identification of iron species within ochres, Mooney et al. (2003) showed that the study of ochres' magnetic properties may even lead to the identification of their provenance. Finally, in the frame of LIBS (laser induced breakdown spectroscopy), the surface of a sample is irradiated with a nanosecond laser pulse leading thus to the formation of a plasma; the latter emits radiation that is characteristic of the elements that are present in the sample under investigation (Pessanha et al. 2012). This technique has been also employed in the frame of pigments analytical investigation (Burgio et al. 2001; Lazic et al. 2018; Botto et al. 2019). Besides, a notable advantage of LIBS over other elemental analysis techniques (e.g., XRF) is the possibility to readily acquire depth resolved compositional information that very much facilitates the analysis of multilayered samples (e.g., paintings) (Pospíšilová et al. 2018). A couple of other spectroscopic techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) will be mentioned in the subsection that deals with the provenancing of ochres (6.4).

Microscopic techniques

Polarized light microscopy (PLM) is regarded as a powerful analytical technique for pigment identification, as it can distinguish pigments on the basis of their color, particle size and shape, and crystal habit (Petraco and Kubic 2003; Helwig 2007; Siddall 2018). Eastaugh et al. (2008) provide an extensive and detailed reference database on PLM that deals with most of the known pigments. Moreover, mere observation of polished sample cross-sections under an optical microscope may yield important information pertaining to pigments identification, and for this reason, optical microscopy (OM) is routinely employed in most of the archaeometric studies of pigmented items.

In the case of scanning electron microscopy (SEM), a beam of accelerated electrons is used for the formation of images (Goodhew et al. 2000; Egerton 2005); therefore, samples can be observed at relatively high magnifications (up to $150{,}000\times$) and with high lateral resolution, while the generated images are of notably large depth of field; in addition, through the combination of EDX detectors (see "X-ray spectroscopy"), the simultaneous estimation of localized elemental compositions is also possible (Adriaens and Dowsett 2004). Another very interesting feature of many SEM devices is the possibility to select between various detectors for image formation. For instance, the topography of the analyzed sample is revealed when the secondary electrons (SE) detector is used, while the backscattered electrons (BSE) detectors allow for the differentiation of the observed phases on the basis of the atomic number of their constituent elements (the higher their atomic number, the brighter they appear) (Fig. 11) (Egerton 2005). The latter detectors often allows for the spotting (through contrast differentiation) of individual idiomorphic (in terms of composition) grains, whose presence are sometimes of decisive importance for provenancing ochres (Mastrotheodoros et al. 2021).
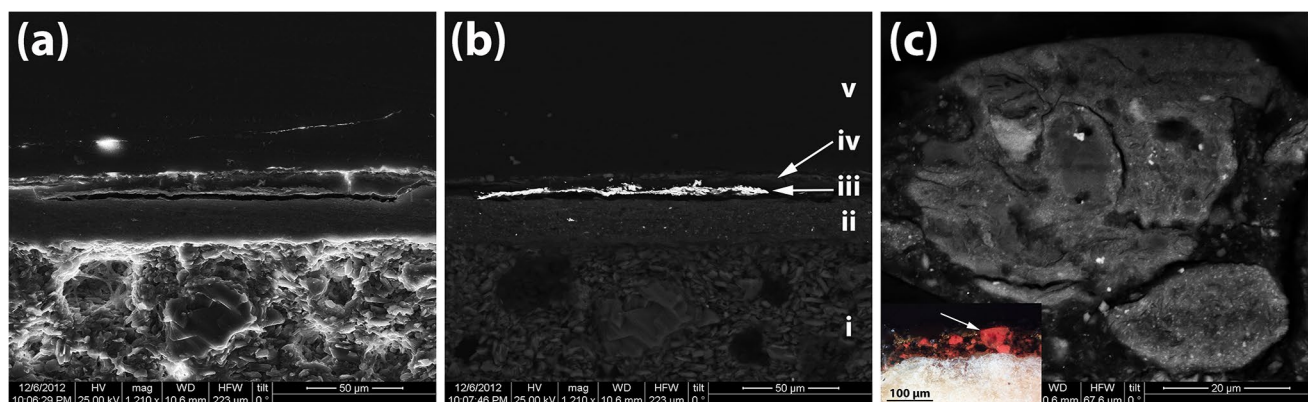

Fig. 11 **a** and **b** Sample from a sixteenth century Greek icon, gilded highlight; the same cross-section as viewed via SE (**a**) and BSE (**b**) SEM detectors (i, gesso ground; ii, bole; iii, gold leaf; iv, varnish; v, epoxy resin). **c** Sample from a seventeenth century Greek icon; composite red ochre grain as seen through the BSE detector (insert: same grain under OM). Images belong to the authors

However, the chambers of most SEM devices are rather small, and this imposes certain limitations as regards the dimensions of the samples that can be examined. Nevertheless, the possibility to simultaneously investigate the elemental composition of individual pigment grains and to observe their micromorphological features is extremely useful when it comes to ochres' identification. Besides, SEM–EDX (often supplemented by a spectroscopic technique that leads to structural identification, e.g., μ-XRD or μ-Raman) is routinely employed in pertinent studies (see, e.g., Genestar and Pons 2005; Elias et al. 2008; Aliatis et al. 2010; Gliozzo et al. 2012; Lehmann et al. 2017; Kostomitsopoulou Marketou et al. 2019, Mastrotheodoros et al. 2021).

Finally, transmission electron microscopy (TEM), which employs an accelerated electrons beam for image formation, allows for the observation of samples with magnifications reaching up to 10^6 times (Goodhew et al. 2000; Egerton 2005). However, as electrons are strongly scattered within matter, the samples need to receive a special pre-treatment prior to their TEM examination in order to be transformed into extremely thin sections. The atomic-scale resolution of TEM permits the observation of individual crystallites and, hence, offers a deep insight into pigment structure. For instance, Pomies et al. (1999) were able to differentiate natural from artificial (: heated goethite) hematite on the basis of the distinct porous nanostructures of the latter, while several other authors have hitherto employed TEM for the characterization of ochres (see, e.g., Chalmin et al. 2003; Elias et al. 2006; Cavallo et al. 2018; MacDonald et al. 2019).

Provenancing ochres

Studies of ochre outcrops have shown that there exists geochemical variability between various sources (e.g., Dayet et al. 2019, MacDonald et al. 2013, Zipkin et al. 2017, Zipkin et al. 2020); hence, in principle, one may reach to provenance determination through the assessment of ochre compositional data (often by applying statistical data treatment, e.g., multivariate statistics). The relevant approaches are commonly based largely on the estimation of the elemental compositions (major, minor, and trace elements) of geological sources in order to build up databases to be used as references for archaeological ochre samples investigations (Popelka-Filcoff et al. 2007, MacDonald et al. 2011, Velliky et al. 2019). In most of the pertinent studies, scholars have been focusing on the determination of trace elements concentrations using various analytical techniques such as neutron activation analysis (NAA) (Popelka-Filcoff et al. 2007, MacDonald et al. 2011, MacDonald et al. 2013, Velliky et al. 2019), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Bu et al. 2013, Scadding et al. 2015, Zipkin et al. 2017, Zipkin et al. 2020), and PIXE (Creagh et al. 2007, Beck et al. 2011).

The identification of the mineralogical composition of ochres is another essential step towards provenance assessment (Hradil et al. 2003). Elias et al. (2006) highlight the relevance of the nature, quantity, and size distribution of white loads with the provenance of a given ochre, while the possibility to correlate an ochre's matrix with its provenance is also noted by Montagner et al. (2013). It is worth noting that Dayet and co-authors (2019) reached a provenance suggestion through SEM–EDS, XRD, and Raman analysis of ochre and reference samples, while Bonneau et al. (2012) suggested a possible source of the studied red ochre largely on the basis of the detection of a single fingerprinting mineral. The stable oxygen isotope ratios of quartz have been also exploited as provenance markers for ochres (Smith & Pell 1997).

Nevertheless the provenancing of ochres is a rather challenging task, and it should be kept in mind that trace elements will not be present at the same level in different phases. Therefore, separation processes affect the ratio of phases in a natural ochre, and, hence, they modify the absolute and relative levels of the trace elements, something that needs to be taken into account in ochre provenance studies. For instance, strontium sulfate is co-precipitated upon gypsum formation (Rosell et al. 1998, Franceschi & Locardi 2014); therefore, Sr is present in gypsum which is a rather common component of several natural ochres. Moreover, in the frame of painting practices, ochres are customarily mixed with other pigments/inert materials; therefore, when analyzing particular painting samples, one may not reach a sound identification of an ochre's elemental or/and mineralogical composition. Similar difficulties may be faced even when analyzing bulk pigment specimens, as the habit of intermixing ochres from various sources (or adding minerals in single-origin ochres) was practiced since the Paleolithic times (Helwig 2007).

Good practice

A preliminary and rapid assessment of ochres can be readily achieved by various non-invasive analytical techniques, such as X-ray fluorescence and FORS. However, the in-depth investigation of ochre pigments requires the combination of structural analysis techniques (e.g., XRD, Raman) and microscopy (i.e., OM, SEM, TEM): structural analysis allows for the identification of the coloring Fe oxides/oxy-hydroxides and accompanying minerals, while microscopy reveals the pigments' micromorphological features, leading thus to, e.g., differentiation between natural and artificial iron oxides and assessment of pigment's processing. In fact, the combination of multiple techniques is often inevitable, and there are several instances of successful ochre identification achieved through the combined employment of various spectroscopic techniques (e.g., Cloutis et al. 2016, Marcaida et al. 2019).

On the other hand, the determination of ochre provenance is a more challenging task. Definitely, the type and quantity of the accompanying minerals/phases that are present in an ochre sample can provide strong hints towards specific geological sources (Hradil et al. 2003; Elias et al. 2006). However, ochre provenance studies are mostly based on high accuracy and high precision elemental analysis techniques that allow for the determination of a plethora of chemical elements in concentration down to trace element levels (Popelka-Filcoff et al. 2007; MacDonald et al. 2013; Scadding et al. 2015; Zipkin et al. 2020). Nevertheless the various types of ochre processing (e.g., levitation, mixing with other substances) may have a considerable effect on both trace element profile and mineralogical composition, and this must be kept in mind when trying to assess the provenance of pigment samples on the basis of raw/geological ochres analyses databases.

Concluding summary of key concepts

Natural Fe-based ochres have been widely employed for artistic, decorative, medicinal, and other purposes since prehistoric times. The main coloring components of ochres are various Fe(III) oxides and hydroxides; grain size along with the type and content of accompanying minerals are the major factors that affect the color of an ochre. Availability, stability, and the wide range of colors/hues are some of the reasons why ochres have found such an immense application in painting. Certain artificial ochre pigments were manufactured during antiquity, yet the large-scale production of corresponding pigments started towards the end of the eighteenth century; soon after, these pigments gained wide circulation among painters and craftsmen and largely replaced natural ochres.

The positive identification of ochres' coloring compounds (i.e., type of Fe oxides/oxyhydroxides) is a rather straightforward process and can be approached through the employment of various analytical techniques. However, the definite identification of an ochre pigment requires combination of structural analysis techniques (e.g., XRD, Raman) and microscopy (e.g., OM, SEM). Thus, one may identify the crystalline and amorphous phases and record the micromorphological characteristics of the corresponding grains. The latter are of enhanced significance when it comes to differentiate between natural and artificial iron oxides and often allow for an assessment of the degree and type of processing of a pigment. The natural ochres have been widely used from prehistory up to the modern times; therefore, they cannot be (at least routinely) used for dating purposes. However, the identification of Mars colors can be (occasionally) used as a terminus post quem. Finally, the assessment of ochres' provenance requires precise determination of (a) the type and quantity of the minerals present in an ochre and (b) the ochre's elemental composition down to trace element level; (a) and (b) rely largely on pigment's processing (e.g., levitation and mixing), and this complicates the provenancing of ochre pigments.

Data availability Data sharing is not applicable as no new data were created or analyzed in this study.

Code availability Not applicable.

Declarations

Competing interests The authors declare no competing interests.

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APPENDIX 1
KEY GRECO-ROMAN LITERATURE ON OCHRES

Important references to ochres in two key Greek sources (Theophrastus and Dioscorides) and two key Roman Sources (Vitruvius and Pliny) are summarized, without substantial overlay with the contents of other sections of this work.

THEOPHRASTUS

Theophrastus wrote at about 310±5 BC the work De Lapidibus and in section 49 states that he will refer to the qualities of the earths used as colors (pigments) by the painters (γραφεῖς). Then he makes detailed reference to miltos (natural and artificial) and ōchra products in sections 51 to 55. The following are the key points:

(a) Ōchra (= yellow ochre): 1) yellow ochre is abundant 'athroa' i.e. found in masses (or in abudance); 2) yellow ochre can replace orpiment (in painting), though the two *appear* to differ as regards color; 3) in some mines, in Cappadocia and elsewhere, miltos and ōchra are found together and a lot of yellow ochre is dug up.

(b) Miltos (= red ochre): 1) many red ochres exist; yet the best miltos comes from the Kea Island; 2) Kean miltos is found both in an iron mine and alone (i.e. in a mine where no smelting is applied), while there is also a Lemnian miltos and a Sinopic miltos; 3) painters use miltos as a flesh-color pigment; 4) the Sinopic miltos exists in three varieties: (a) a very red (σφόδρα) miltos, (b) a pale/light red (ἔκλευκος) miltos, (c) an intermediate of (a) and (b); 5) the intermediate red miltos of Kea, the one so-called 'self-sufficient', does not have to be mixed, while mixing is necessary for the other two; 6) One can also produce an artificial miltos by heating, in new earthen vessels covered with clay, a yellow ochre to the point it becomes crimson (πεφοινιγμένη) and the hotter the fire the darker the attained color; yet the product is inferior to [good quality] natural miltos.

VITRUVIUS

In De Architectura, Vitruvius reports, at around 30 BC, the architecture-related knowledge of the Romans and the Greeks and includes important references to materials. In Book VII Vitruvius deals with the ochre-related subjects in three Chapters. The key points per chapter are as follows:

(a) Chapter VII. The best yellow ochre originated from Attica (Laurion mines); it was used extensively, especially in frescoes, and has been exhausted. Red ochre is widely available and the best varieties are those from Sinope, Egypt, Balearides Isles and Lemnos; Romans offered the revenues of the Lemnian product[s] to the Athenians, possibly at about 167 BC (according to F. Granger, the Editor of the 1934 Loeb translation of De Architectura).

(b) Chapter XI. A yellow ochre when roasted and then quenched in vinegar develops a purple color.

(c) Chapter XIV. Some stucco painters imitate the color of Attic ochre by boiling dried violets in a vessel with water and pouring of the resulting water on creta (= chalk); the latter chalk when ground resembles Attic ochre.

DIOSCORIDES

Dioscorides reports medicine-related Knowledge of the Greco-Roman world up to the middle part of the 1st c. AD and write at about the same time as Pliny. Dioscorides (in De Materia Medica) describes medicinal substances in five volumes; ground inorganics, some of which are also used as pigments, are described in Volume E of the work. Dioscorides. Lemmas of present interest are those pertaining to rust (E.80) and iron metallurgy slag (E.80), yellow ochre (E.93), red ochre (E.96), Lemnian earth (E.97), misy and (E.100) sori (E.102), hematite (E.126), magnetite (E.130). The following are the pieces of information of main interest for the present work:

(a) The yellow ochre of choice (E.93) is described as 'μηλίνη' (quince-yellow) and 'κατακορής' (richly colored); also, it should be light, brittle and free of stones.

(b) Sinopic miltos has a liver-like hue. Sinopic miltos is found in Cappadocian caves and, following filtering, is sold in the port of Sinope (E.96). Also, we can infer today that Sinopic miltos is a hematite-based red ochre, as Dioscorides states that hematite stones are found within Sinopic ochre (E.126). The last piece of information is important as it follows that red Sinopis can hardly be a pigment other that red ochre, despite some suggestions of our era that Sinopis was e.g. cinnabar-based and not a hematite-based pigment.

(c) A 'tectonic miltos' (a red ochre good for masonry/architectural purposes, E.96) is inferior to sinopic miltos in all respects. The best tectonic miltos comes from Egypt and the West of the Iberian Peninsula; the latter is prepared upon firing of magnetite (loadstone).

(d) The Lemnian earth is extracted from a cave-like hollow and is mixed with goat's blood (E.97); Galen later stated (De Simpl. Med., 9.2) that he interviewed knowledgeable people of Lemnos and found no basis for the latter claim of Dioscorides.

(e) The best hematite comes from Egypt (E.126).

(f) Some people sell burnt magnetite as hematite (E.130).

PLINY

Pliny records the 'Natural History' knowledge of the Greco-Roman world up to the middle part of the 1st c. AD. He makes several statements pertinent to ochres and related materials in Natural History (NH), Books XXXIII to XXXVII; he offers information about materials such as ochre and sil, rubrica, sinopis, Lemnia rubrica and bolos, hematite and hematite magnet, sandyx and syricum and misy and sori. The information offered by Pliny is rich but, unavoidably, less homogenized than that of specialized antiquity sources. The most important of the pertinent pieces of information follow.

(a) Red ochre displaced cinnabar as a red pigment in cases that the color of the cinnabar pigment was considered too harsh and also was found difficult to preserve (XXXIII.117) Red ochre and yellow ochre (also sandyx and syricum) are among the so called somber ('austeri') colors (XXXV.30)

(b) The best kind of Sinopic red ochre is used for painting with a brush or for wood coloring (XXXV.31). Cicerculum, which is a deep red ochre imported from Africa, is appropriate for panels (XXXV.31). Native rubrica maybe found in iron mines (XXXV.35)

(c) 'Schistos' (which is 'closely related to hematite' and, possibly, a FeOOH-based material) is crocus (= saffron) colored (XXXVI.145). A hard Arabian ''hematite'' (possibly goethite or a 'limonite'-type of ore) might leave a saffron-colored smear (XXXVI.147). A black hematite, in particular an exceptionally heavy and hard variant known as 'androdamas' (man tamer) leaves a blood-red smear (XXXVI.146, 147). A liver-colored ('hepatites') hematite becomes 'miltos' when roasted (XXXVI.147). While some of the hematites of Pliny might not be present-day hematites, Pliny is right in that the particular mineral is found in a broad variety of forms; Sotacus of Carystos, an older authority and one of the sources for Pliny, lists five kinds ('genera') of hematite-proper (XXXVI.146).

(d) A form of hematite *magnet* ('haematites magnes', XXXVI.129) is known to exist. From today's perspective such a material can be a black hematite mineral without magnetite or a rock containing hematite and magnetite or even a combination of hematite and FeO(OH). In one case of detailed description, the 'haematites magnes' rock is (predominantly?) blood-red and can be ground to give both a blood-red powder and a saffron-colored powder.

(e) Bolus / bolos (< bōlos, Greek) is an earth that is found near the Iberian Ebro river and has the form of globules (XXXVII.150). From today's perspective, the latter material might be on of the red-ochre type, such as the 'Armenian bole'.

APPENDIX 2
METHODOLOGY

Spot XRF analyses (figure 6c) were performed using a milliprobe XRF spectrometer equipped with a Rh-anode X-ray tube (50W, 50kV, 75μm Be window), a Si-PiN detector (XR-100CR, Amptek Inc.) with a 500-μm nominal crystal thickness (resolution: 165 eV FWHM at Mn K_α), a detector power supply (PX2CR, Amptek Inc.) and a low power multichannel analyzer (MCA-8000A, Amptek Inc.). Images shown in figures 7a and 10c were acquired through an optical microscope (Leica, DMRPX). The determination of the lateral distribution (map) of iron (Fe) shown in figure 6a was achieved through the employment of a M1-Mistral tabletop spectrometer (Bruker) which is equipped with a micro-focus X-ray tungsten tube and a high-resolution SSD detector.; the relevant analyses were conducted by Professor D. Anagnostopoulos and PhD candidate A. Asvestas from the Materials' Science and Engineering Department, University of Ioannina. The SEM images shown in figures 4a, 4c, 7b, 10a, 10b & 10c were acquired through a Quanta Inspect D8334 (company FEI) SEM-EDX device, while EDX analyses (figures 5-right, 7c & 11) were conducted using the built-in SEM's 'Genesis-Spectrum' software (EDAX Company). Finally, μ-Raman analyses (figure 9) were conducted through a Renishaw inVia device, using a low power (~0.01-1mW) 514nm laser.