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ASSESSMENT OF THE PRODUCTION OF ANTIQUITY PIGMENTS THROUGH EXPERIMENTAL TREATMENT OF OCHRES AND OTHER IRON BASED PRECURSORS

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ABSTRACT

In this work we explore the effects of various grinding and thermal-oxidative treatments applied to natural and artificial iron-based materials available (or related to those available) during GraecoRoman antiquity. The raw materials examined are: (a) commercial natural iron pigments (ochres, natrojarosite, caput mortum), (b) artificial melanterite ($FeSO_4 \cdot 7H_2O$), (c) mineral pyrite (FeS_2) and mineral metallic hematite.

Additionally explored are: (a) the non-attested in surviving sources, yet highly probable during antiquity, route of pigment preparation from iron (or steel) plates exposed to vinegar vapors, (b) a Vitruvius recipe for purplish pigment via vinegar quenching of hot ochre.

We obtain oxide pigments with colors ranging from yellowish and red to brownish and purplish. The puzzling variation of colors obtained by subjecting iron-oxide containing materials to identical oxidative heat treatments is found to be explainable on the basis of starting grain size and possible size modifications. We also show, by using highly purity starting materials, that purplish colors obtainable in certain cases by heat treatment do not necessitate, as often claimed, the presence of impurities such as manganese etc. A framework of antiquity color possibilities for iron-oxide based pigments obtainable under the conditions explored is included. All samples prepared are examined via scanning electron microscopy for micromorphology coupled with EDAX for composition, and X-Rays Diffraction for mineralogy.

KEYWORDS: ochres, hematite, grain size, color, antiquity pigments

INTRODUCTION

During GraecoRoman antiquity, various substances were used as pigments; the available range at the end of that period, also served the needs of medieval times, with a number of additions (e.g. high quality ultramarine), few losses (e.g. Egyptian blue) and case-specific adjustments imposed by changes in the techniques of pigment application.

In the quest for expansion of the available color palette, the modification of proper raw materials was frequently involved; we know today that successful antiquity attempts were a reflection of changes having either a chemical (e.g. synthesis of Egyptian blue, artificial minium and artificial cinnabar) or a physical chemical character (e.g. formation of lakes via sorption and occasional strong color shift upon particle size modification). The antiquity arsenal of material modification practices was limited and rarely included anything beyond grinding (dry or with a liquid), mixing, heating (either in an oxidizing or in a reducing atmosphere) and interaction with a few liquids, vinegar being among the most potent and popular latter ones. The quest was continuous and a fully empirical one; prevailing theoretical views about the nature of matter (such as variations of the 4th century BC views of Plato and Aristotle) could only offer misguidance and eventually functioned as a prestigious background contribution to the obsession-driven Alchemy in her Graeco-Egyptian and later versions.

While the present work focuses on GraecoRoman antiquity, our introductory section is enhanced by medieval references, as the surviving Graaeco-Roman records are far from satisfactory. One of the most important, yet frequently overlooked, GraecoRoman sources is the fifth volume of 'De Materia Medica' (by Dioscurides) which emphasizes inorganics but for a different application (: pharmaceutical preparations). Yet, luckily for us, Dioscurides sprinkles, here and there, information directly pertinent to pigments. Still, the occasional generosity of Dioscurides is no substitute for an antiquity source having a similar breadth, a focus on pigments and an author with a first hand experience. The latter is absent in the case of Pliny who in his Natural History (especially volumes XXXIV and XXXV) offers a, far for critical, compilation of heterogeneous material.

Among iron-oxide based pigments, *natural* ochres are a perennial part of the palette of painting; they are also the subject of current research of archaeological and geological interest (Popelka-Filcoff *et al* 2007, Popelka-Filcoff *et al* 2008, Iriarte *et al* 2009). During historical times, the natural ochres supply half of the celebrated and frequently debated four-color palette of key Greek painters of the classical and Hellenistic times; see for example Pliny, Natural History, XXXV.50, where Sinopian red and yellow ochre are considered. Surviving references to the *modification* of ochres start with Theophrastus, who describes, at about 315-312 BC, the production, supposedly known since only about the middle of 4th c. BC (Pliny, Natural History, XXXV. 128, 130), of an inferior substitute for red 'miltos' (ruddle) via calcination of natural yellow ochre. According to Theophrastus (De Lapidibus, 53-54), variations in the oven temperature may result in the alteration of the final hue of the pigment. In the same discussion, Theophrastus describes three hue grades of natural 'miltos': deep red, pale red and medium red. The first two grades require adjustment through mixing, while the third does not and, hence, it is called 'autarkēs' (self-sufficient). Dioscurides (De Materia Medica, E.96) refers, at about the middle of 1st c. AD, to the conversion, via heating, of yellow ochres, mined at the West of the Iberian peninsula, to 'miltos'. A further option is briefly described by Vitruvius and Pliny. Vitruvius, writing at about 30 BC, refers (De Architectura, VII.XI.2) to the quenching of hot ochre in vinegar, in order to obtain a purple ('purpureo colore') pigment; Pliny describes (Natural History, XXXV.38), at about 77 AD, an almost identical process for a purple ('purpurea') pigment 'made in Rome'.

Another, popular and subject to generalization, antiquity process for the production of artificial pigments was the oxidation of thin metal sheets via exposure to vinegar vapors or, in other versions, via proper direct contact of metal sheets with liquid vinegar. The vinegar route, amply reported for lead and copper, led to highly popular pigments, white ceruse and green verdigris, respectively (e.g. Theophrastus: De Lapidibus, 56-57; Vitruvius: De Architectura, VII, XII.1; Dioscurides: E.88 and E.79, Pliny: Natural History, XXXIV. 175). Instead of vinegar, one can use certain other products and by-products of grape-processing; even versions employing urine are known and Theophilus offers handy medieval examples (De Diversis Artibus, I.XXXV and I.XXXVII). Descriptions of pigment formation based on the controlled corrosion of lead and copper extend beyond medieval times and, overall, span a period in excess of 2000 years.

Given the vast success of the ceruse-from-lead and verdigris-from-copper pigments, there can be no doubt that the outcome of the metal/vinegar method was also investigated intensively for, at least, the cases of the remaining simple (or lightly alloyed) solid metals that have been isolated during antiquity. The remaining simple or mildly-alloyed solid metals known during GraecoRoman antiquity are: (a) gold, for which no product will result, (b) pure tin, for which no product of pigment interest will result (for the potential interest of certain tin alloys see below), (c) silver, for which nothing of pigment interest is expected (yet, see below), (d) iron (and steel), for which products of pigment interest can easily result.

In the case of silver, there is the still unresolved issue of 'silver blue' (Thompson, 1956, Ball, 2003), supposedly the result of some, simple or complex version, of silver plate exposure to vinegar. A simple description for the preparation of the elusive 'silver blue' is offered by the, recorded around 1160±20 AD, 'recipe ii' of the medieval recipe compilation known as Mappae Clavicula (Smith & Hawthorne, 1974); we are not aware of any clear hints for a closely related silver-based recipe in pre-medieval sources. Today, the 'silver blue' claims are usually attributed either to the role of impurities (including but not limited to copper) or to the perpetuating influence of some unsubstantiated alchemical theoretical view.

For the sake of completeness of considerations pertaining to vinegar (or urine) processing, it is noted that certain alloys might offer additional pigment preparation options. For example, Pb/Sn alloys are, at least in principle, potential raw materials for yellow lead stannates; the latter compounds are currently documented as glass colorants from 1st c. AD, while current documentation of their availability as free pigments is only from medieval times [Kühn, 1968, Biek and Bayley, 1979 and Heck et al., 2003]. The origin of the yellow lead stannates, for each application and also at different periods, is debated. The involvement of Pb/Sn alloy vinegar processing (plus firing) might deserve consideration as an additional, at least occasional, preparation method.

Let us now turn our attention to the case of iron (or steel)/vinegar, which is the only safe (as regards outcome) remaining possible case of the simple (or lightly alloyed) metal / vinegar route with products of pigment interest. As it is experimentally documented in later sections of this work, the iron (or steel) exposure to vinegar can lead, without any technical difficulty, to products which are of substantial practical pigment interest, either in the as-prepared oxidized state or upon subsequent heat treatment. Admittedly, the same colors can be obtained by employing various natural ochres as raw or final materials. However:

(a) Iron (steel) and vinegar were available ‘everywhere’ (and to ‘anyone’), while good to high quality natural ochres were not equally accessible, as suggested by the fact that, during GraecoRoman antiquity, good ochres had a name of origin; e.g. the yellow ochre from Attica (Vitruvius, VII.VII.1) and the Sinopian (ultimately: Cappadocian) miltos (Dioscurides, E.96) were widely appreciated.

(b) Available natural ochres cannot always serve (at least as *single* raw materials) as sources of the color spectrum obtainable by the iron-vinegar route; for example, a natural red ochre can not be converted, at least in a simple manner, to a yellow ochre and, also, some yellow ochres can not become, upon firing, sufficiently red or darker (see below).

(c) The GraecoRoman quest for iron-oxide based, deep earthy hues through ways alternative to native hematite oxides and fired yellow ochres is substantiated by Dioscurides. Dioscurides describes (E. 126 and E.130) a, frequently applied, oxidative thermal conversion of magnetite (Fe_3O_4), an esteemed mineral, to a hematite-type of material.

For whatever reasons, no explicit antiquity reference to the obviously attractive option of the iron/vinegar route to artificial ochres survives. Obliquely related are:

(a) Various pharmaceutical preparations where fine iron (or, more often, iron rust) is mixed with vinegar and additional ingredients; several such recipes can be found in the works of Dioscurides (1st c. AD), Galenus (2nd c. AD) and later followers.

(b) A Greek recipe [Berthelot and Ruelle, 1888] calling for the addition, in a glass container to be sealed and left in the sun, of iron scales to vinegar, which, nevertheless, contains other dissolved ingredients. The recipe can be compared, in terms of style, to 3rd c. AD recipes but survives in a, heterogeneous yet mostly alchemical in spirit, recipe compilation from Byzantine times; recipes found in the same compilation in the vicinity of the one of interest bear traces of a date around 7th c. AD. The recipe in discussion pertains to the field of stone imitation through artificial coloring and, hence, is also conceptually close to the pigment route in discussion.

Another potential way of expanding the range of iron-oxide based colors is the application of grinding and/or heating to obvious mineral iron sources such as pyrite (FeS_2), melanterite ($FeSO_47H_2O$), hematite (Fe_2O_3) etc. Here, again, it is difficult to recover enough details as regards the variety and history of pertinent practices, on the basis of surviving records alone. In addition to the aforementioned reference of Dioscurides (E.126 and E.130) to magnetite firing, the following are among the most pertinent references:

(a) Dioscurides (E.103) refers to pyrite ('pyritēs') converted, upon long firing, to a material with a miltos-type color ('miltōdēs khroa'); yet, it appears that the starting material is the mixed $CuFeS_2$ rather than the simple FeS_2 sulphide and the calcined product includes copper. Dioscurides also states that for certain pharmaceutical applications calling for calcined 'pyritēs' some merchants offer instead a similarly colored (but less effective) calcined ochre.

(b) A clear pertinent description of the melanterite route is found in a medieval (probably ca. 1122 AD) source (Theophilus, III.40): melanterite ('atramentum', green vitriol) is subjected to oxidative heating and eventually converts to red ('rubeum colorem') hematite. In the case of Theophilus, this might be only a secondary route of producing hematite, needed for a specialized metal-surface preparation process where enhanced fineness of hematite particles appears to be important. In other sections of the same work (Books I, II and III), when a hematite pigment is employed, it is either stated that the material results from the firing of an appropriate ochre (Theophilus, I.3 and I.23), or its origin is left unspecified (e.g. Theophilus, I.12, I.13).

In view of the accessibility of raw materials, the simplicity and obvious character of necessary processing and the pigment interest of the final, highly reproducible and high-purity (: in terms of iron oxide content), products, the lack of surviving GraecoRoman clear reports to iron-based pigments through iron (/ steel) vinegar processing or the aforementioned simple treatments of a host of iron minerals might well be accidental, almost amounting to a proof of the incompleteness of pertinent records. Firing of certain iron compounds (other than oxides and oxihydroxides) is a common current practice for the preparation of artificial pigments based on iron oxide but need not be limited to relatively recent times. As a matter of fact, it is practically a fully safe assumption that all materials available (or easy to prepare) during antiquity have also been subjected to firing, at least by the end of Hellenistic times. It is also instructive to consider the number of components involved in pharmaceutical preparations described in the five volumes of the Dioscuridean 'De Materia Medica'. These volumes include an impressive array of 3 to 5-component recipes, with little beyond a purely combinatorial logic revealed, at least up to the level of 2-component combinations. Then, it can be guessed that by the first century AD, all possible, or at least all 'reasonable', 2-component (or quasi 2-component) combinations (hence, among them, all combinations of simple metals and their key alloys with vinegar) have already been explored (and those of apparent further interest have been subjected to firing), despite the implied need for a staggering number of tests.

The consideration of the aforementioned antiquity references (or, in other cases, the lack of clear references to undoubtedly applied, at least occasionally, practices) and exposed auxiliary materials-based reasoning motivated the experimental research reported herein. In addition, while partial connections of parameters explored here (e.g. between grain size and color, between grain size and firing temperature and between argillaceous content and color achievable upon firing) have been noted before in different works (see our Discussion section for pertinent references), there is, to the best of our knowledge, no clear synthesis allowing for the understanding of the bewildering variety of colors observed upon processing of various iron (III)-oxide pigments.

As regards materials considered herein, we study: (a) artificial ochres produced via the vinegar route from three iron-metal precursors, (b) seven modern iron-oxide based pigments designated as natural ones, (c) iron oxides produced through treatments of pyrite and metallic hematite minerals and a commercial artificial version of hydrated iron (II) sulfate.

Pigment modifications were attempted via firing at 3 temperatures (which, practically, exhaust the temperature range acessible during GraecoRoman antiquity), grinding, firing and vinegar processing (both metal exposure to vinegar and quenching of hot oxides in vinegar).

Materials generated were studied via Scanning Electron Microscopy (micromorphology assessment) coupled with EDAX (composition assessment) and X-ray diffraction (crystal structure assessment). Thus, the colour changes after calcination in different temperatures were explained through the investigation of composition, crystal structure and micromorphology.

MATERIALS AND METHODS

A. Materials

Iron-based materials employed in this work fall into four categories. Comments exposing the rationale (in addition to the explanations provided in the Introduction) of choices are included.

(a) Iron-based metal raw materials. Three materials have been chosen: a 1005 (SAE-AISI) steel (C = 0.06 % w/w, Si = 0.045 % w/w, Mn = 0.045 w/w-OX2), a typical unalloyed common cast iron (C = 4.3 % w/w, Si: 1.0 % w/w-OX3) and electrolytic iron (high purity iron-OX4). Obviously all three are modern iron - based materials; yet we find that, despite their substantial variability, the application of the metal/vinegar technique (and calcination extensions) yields quite similar products. Hence, we believe that the yield of the potential application of the same technique to antiquity irons and steels is, more or less, captured. Finally, the employment of electrolytic iron allows for the determination of color trends that are independent of the variety of foreign atoms that might be found in ancient and current irons and steels.

(b) Melanterite (< melantēria, Gk): We have used artificial granular melanterite ($FeSO_4 \cdot 7H_2O$, 99.5 % purity) from Merck. We have chosen an artificial version that is a well-defined product as there is some vagueness about the character of antiquity 'melantēria' of mineral origin. Today it is believed that ancient 'melantēria' was frequently green vitriol, i.e. hydrated iron (II) sulfate, though it was occasionally mixed with (or replaced by) different sulfates or confused with other, difficult to identify today, products, such as, for example, those described by Dioscurides (E.101). During antiquity, melantēria was a widely spread 'shoemaker's black' and, thus, a rather common product. Pliny reports (XXIV.112) that 'atramentum sutorium' is also used for the adulteration of Rhodian verdigris and, upon firing, the adulterated product displays a red color. The greenish, similar to that of verdigris, color of the original 'atramentum sutorium' and the red color of the fired version of the adulterated product suggest that, at least, the particular 'atramentum sutorium' exhibited color trends compatible to those of iron sulfate.

(c) Pyrite (FeS_2) in natural yellow-metallic cubes and hematite (Fe_2O_3) in natural compact silvery-gray masses. Common mineral versions have been employed.

(d) Commercial natural pigments from Kremer {pertinent information included in parentheses has been provided by 'Kremer pigmente'}: 1. Ochres: Gold ochre (N40194: Kremer's product classification number), Burgunder (yellow) ochre (N11573), Cyprus Jarosite (N17000), Jarosite (N11520), French yellow ochre (mixture of various yellow natural earths, N40010), English red ochre (from English mines, N40351). 2. 'Hematite' (natural mineral hematite, N48600), 'Caput mortum' (burnt umber from Cyprus, N48720).

A reasonably broad range of commercial pigments based on iron-oxides (ochres, 'jarosites', hematite and 'caput mortum') were chosen for the exploration of color and structural trends upon firing or vinegar quenching. Firing explored herein was applied to these pigments in the as received state.

In general, commercial hematite-based pigments might originate from: (I) native hematite sources, (II) firing of certain yellow or orange natural ochres, (III) firing of iron compounds other than those based on iron oxides and hydroxyoxides. We have chosen commercial pigments (d) described as 'Natural', in order to avoid, as much as possible, raw materials or processing contributions totally alien to those accessible during antiquity.

The commercial 'caput mortum' (or c. mortuum or c. mortem) is an iron-oxide based pigment chosen by us on the basis of its distinct hue and not with the intention of comparisons with a particular ancient pigment. The occasionally expressed conviction that there is a well-defined 'caput mortuum antiquity pigment' is not guaranteed; the antiquity depth of the distinction of a family of iron-oxide based pigments with such a name remains unclear. Such a pigment name is not encountered in Latin sources such as Vitruvius and Pliny, medieval Alchemy simply pours confusion and even the details of the 1600-1835 AD period (Harley, 2001) as regards 'caput mortuum' pigments are quite complex and, still, rather uncertain. While today certain iron-based pigments that display purple or violet hues and originate from Roman sites are described as 'caput mortuum' (e.g. Edwards et al., 2002), this remains a current choice of a name, applied (and limited) to an intuitively defined-hue range of Roman pigment artifacts; further, the non-unanimous definition of the latter range is affected by a factor of zero archaeological relevance, namely the commercial 'caput mortum' naming of current pigments.

Finally, we have employed home-made vinegar for the metal/vinegar route and for the 'hot ochre quench in vinegar' process. The vinegar was obtained through natural conversion of wine. The acetic acid content of vinegar was 7.93 gr/100 ml.

B. Processing of Materials

(a) Firing conditions/Heat treatment: Furnace employed is a Heraeus-Rof 7/50 with Thermicon P temperature control unit. The artificial and natural pigments were heat-treated at three different temperatures (700, 900 and 1100 °C) for 2 hrs. Subsequently, the furnace was turned off and left to cool until it reached room temperature. The firing conditions were retained oxidative during the full procedure.

(b) Hot-Pigment quench in vinegar: in the case of yellow and red natural ochres (Kremer) a small quantity of the pigment was removed during the calcination at 700 °C and was immediately quenched in an inert vessel containing 50 ml of vinegar. The pigment was left to settle down, then the vinegar was removed and finally the pigment was air-dried.

(c) Grinding for color assessment: Artificial oxides obtained via the iron (or steel) / vinegar route, as well as the metallic hematite and pyrite minerals, were subjected to intense manual grinding with an agate mortar and pestle before firing. Whenever necessary (: as judged visually), the intermediate (fired) products were ground again. The products from Kremer were already pigment-grade and no further grinding was applied before firing, though fired samples were subsequently grinded. Melanterite was also ground only after firing.

(d) The vinegar route for artificial iron oxides was applied as follows: 150 ml of vinegar were placed in a glass container. Thin sheets of the aforementioned iron-based metals were exposed to the vinegar's vapors (no direct contact of metal and liquid vinegar phase) and the container was sealed. Experiments were carried at a T = 19±1 °C environment and the oxidized product was collected via scraping at 7-day intervals.

C. Characterization

(a) Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectrometry (EDAX): For the micromorphological and quantitative analysis of the pigments a FEI SEM coupled with EDAX was used (model Inspect, with Super Ultra Thin Window). The samples were observed alternatively in the secondary (SEI) and backscattered (BSE) electron mode. The voltage applied on the filament was 25 kV and every spectrum was collected for 100 live sec (Total counts ≈ 30,000).

(b) XRD: For the crystal structure identification a Siemens X D 500 difractometer with a Cu Ka anticathode was used. The voltage was 40 kV and the current 35 mA, while all the diffraction spectra were collected in the range between 2 and 85° (2θ) with a step of 0.04°/2 sec.

(c) Color assessment: The color assessment was made according to the "Munsel soil color chart" (http://www.munsell.eu/html/munsell_color_standards.html). In addition, a GretagMacbeth SpectroEye spectrophotometer was used in order to record the visible reflection spectra of the pigments (see Appendix 1).

RESULTS

1. Artificial iron oxides

The three oxides produced by the different metallic sheets were identified via XRD as goethite while examination in SEM revealed the characteristic needle-like micromorphology (see Fig. 1). They are all characterized by yellow hues, although the product of cast iron appears to be slightly more brownish (see Table 2). They are totally converted to hematite (33-0664 code number of the mineral according to "Powder Diffraction File"-PDF) upon firing at 700 °C and no further crystal structure change is observed at higher firing temperatures (Fig. 1).

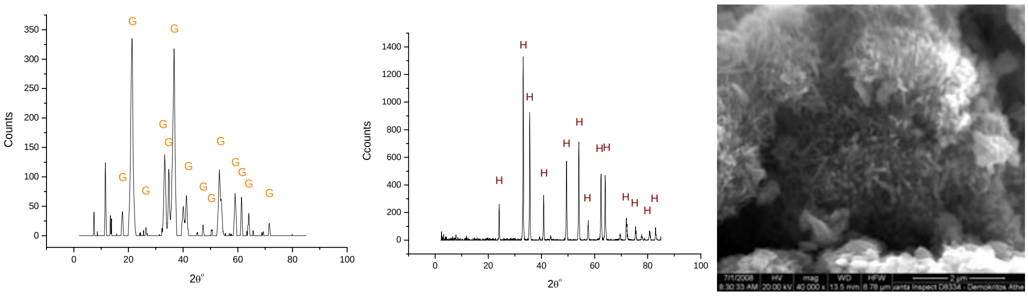

Fig 1: Upper left: XRD pattern of artificial iron oxide before firing, Upper right: XRD pattern of artificial iron oxide after firing at 700 °C, Down: Characteristic micromorphology of goethite (OX2, ETD, 40,000x).

Firing of the three oxides at 700 °C resulted in the production of red-colored pigments. Only the product of the cast iron differed slightly, as it gained a red-brown hue. The SEM examination revealed the total destruction of the initial micromorphology and the formation of new, round-shaped hematite grains with diameters between 0.2 and 0.5 μm (see Fig. 2). The color of the pigments changed significantly upon firing at higher temperatures as it turned deep red at 900 °C and 'violet' at 1100 °C (see Table 2, Fig. 3 and Appendix 1). In addition, the diameter of hematite grains increased: grains with a diameter between 0.4 and 1 μm are formed at 900 °C and even larger ones (diameter: 1.1 to 3+m) are formed at 1100 °C (Fig. 2).

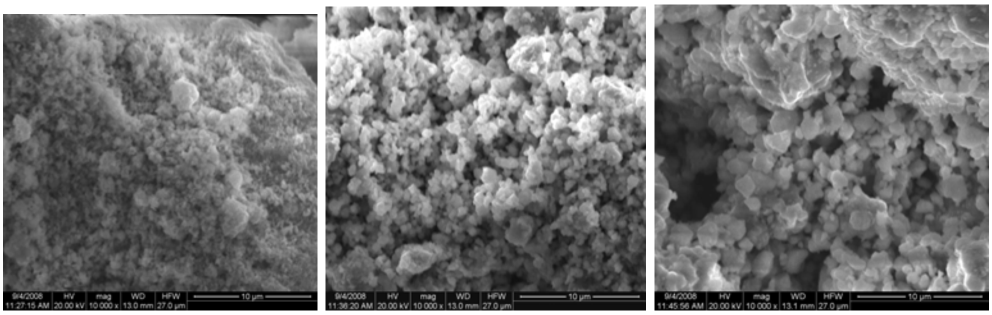

Fig. 2: Hematite grain size differentiation upon firing at different temperatures (OX2). Upper left: grains formed at 700 °C (0.2-0.5 μm, SEI, 10,000x), Upper right: 900 °C (0.4-1 μm, ETD, 10,000x), Down: 1100 °C (1.1-3^{+}μm). (ETD, 10,000x).

Fig. 3: Color changes of the artificial iron oxides upon firing. From left to right: 1: ground version of as-prepared artificial iron oxide (vinegar route, OX2), 2: after firing at 700 °C, 3: after firing at 900 °C, 4: after firing at 1100 °C.

2. *Yellow natural pigments*

The chemical composition (revealed by SEM) of the raw materials is presented in Table 1 while their color (according to Munsel soil color chart) is presented in Table 2. Three of the five yellow ochres exhibited similar color responses upon firing; they all developed reddish hues. It was also observed that the maximum heating temperature applied in this work (1100 °C) resulted in slightly deeper hues (see Table 2 and Appendix 1). As regards crystal structure changes it was found that firing resulted in the transformation of goethite to hematite and the reduction of the intensity of clay mineral peaks; no substantial micro-morphology changes were observed, at least up to a 5000x magnification (Fig 4). Jarosite N11520, despite its commercial name, was found, via XRD probing, to be a mixture of calcite, quartz, goethite and clay minerals (Kaolinite-Montmorilonite). Upon firing, the latter material underwent minor changes in crystal structure and micromorphology. Further, in contrast to the other three yellow pigments, this 'Jarosite' did not turn red upon firing but retained, despite the YR (=yellow-red) Munsel designation of color, a color that can be colloquially designated as 'dull yellowish-grey'.

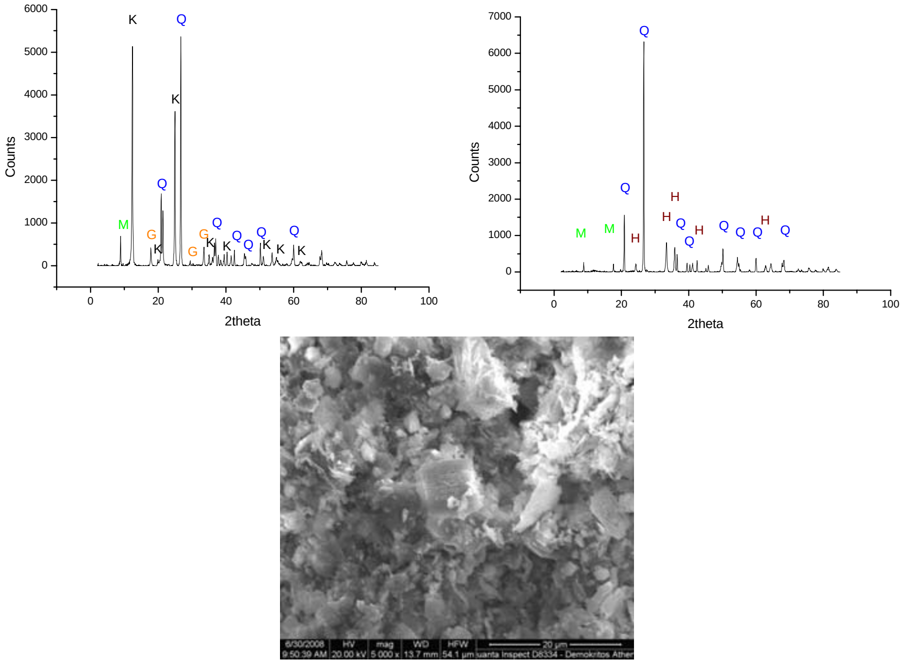

Fig. 4: Upper left: XRD pattern of French Ochre in the as received state (Q: Quartz, K: Kaolin, M: Muscovite, G: Goethite). Upper right: XRD pattern of French Ochre after firing at 900 °C (H: Hematite). Down: Micromorphology of French Ochre (SEI, 5,000x).

On the other hand, "Cyprus Jarosite – N17000" was identified, via XRD, as natrojarosite ($NaFe_3[(OH)_3|SO_4]_2$ - 30-1203) with quartz (33-1161) admixtures, while the SEM quantitative analysis gave iron, sulfur and silica concentrations as high as 43.5%, 28.8% and 20.1% respectively (in w/w % oxides; see Table 1). The color of the product changed significantly upon firing: by firing at 900 °C or higher temperature, Cyprus Jarosite is totally converted from yellow-colored to purple-violet. As expected (in view of the composition of the raw material), the applied firing affects significantly Jarosite's crystal structure and chemical composition: in all three XRD patterns of the calcined pigment (700-900-1100 °C) the main phase identified is hematite (33-0664) accompanied by minor quartz peaks, while the amount of sulfur is reduced with increasing firing temperature. The initial cubic grain-like micromorphology disintegrates during firing and crystals of a new phase, hematite, eventually develop (Fig. 5). The size of the latter crystals is affected by the firing temperature: higher temperatures lead to larger hematite crystals (Fig. 5).

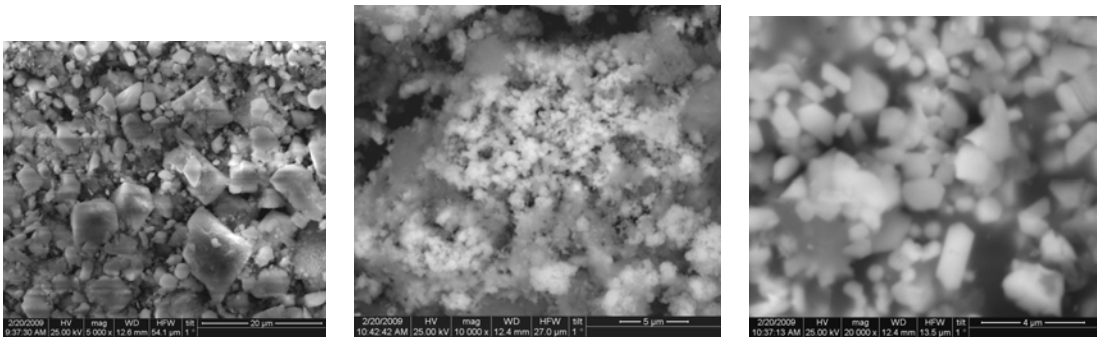

Fig. 5: Upper left: Cyprus Jarosite before firing, (SEI, 5,000x). Upper right: after firing at 900 °C (BSE, 10,000x). Down: well developed hematite grains after firing at 1100 °C (BSE, 20,000x).

All aforementioned pigments were also quenched in vinegar according to the method suggested by Vitruvius (De Architectura, VII.XI.2). Vitruvius states that the pouring of hot, fired ochre in vinegar results in the production of a purple pigment, but we were not able to verify his statement; vinegar quenching did not alter significantly the color of any of the five, originally-yellow pigments (yellow ochres and 'ochres') employed in this work.

Table 1: Chemical composition of the raw materials (w/w %)

Name	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	SO_3	Fe_2O_3
F.O.	-	-	21.6	55.5	1.2	1.3	-	18.5
J.	-	1.0	20.2	48.0	0.5	14.2	-	14.2
C.J.	5.4	-	0.3	20.1	0.6	0.4	28.8	43.5
B.O.	-	0.6	17.4	45.8	1.5	0.2	-	33.8
G.O.	-	1.7	18.0	59.2	2.7	1.6	-	15.6
C.M.	-	1.2	3.1	4.9	-	1.8	4.5	85.4
R.E.O.	-	1.0	4.3	5.4	1.0	0.7	-	88.3
H.	0.7	-	2.2	2.9	-	2.4	1.8	90.0
OX2	-	-	-	-	-	-	-	100.0
OX3	-	-	-	1.5	-	-	-	98.5
OX4	-	-	-	-	-	-	-	100.0
mH.	-	-	-	-	-	-	-	100.0
FeS_2	-	-	-	0.8	-	-	60.4	38.8
FeSO	-	-	-	-	-	-	72.6	27.4

Abbreviations: F.O.: French ochre (4001), J: Jarosite (11520), C.J: Cyprus jarosite (17000), B.O: Burgunder ochre (11573), G.O: Gold ochre (40194), C.M: Caput mortum (4872), R.E.O: red english ochre (40351), H: hematite (4860), OX2: steel, OX3: cast iron, OX4: electrolytic iron, mH: metallic hematite, FeS_2*: pyrite, FeSO: melanterite (*$FeSO_4 7H_2O$*).*

Table 2: Color of the as received pigments and after their respective heat treatment (according to the 'Munsel soil color chart').

Name	As received	700 °C	900 °C	1100 °C
OX2	10YR 5/6	10R 3/4	10R 3/2	10R 2.5/1
OX3	10YR 4/4	2.5R 3/6	10R 3/2	10R 2.5/1
OX4	10YR 4/6	10R 3/4	10R 3/2	10R 2.5/1
F.O.	10YR 7/8	2.5YR 5/8	2.5YR 5/8	2.5YR 4/8
J.	10YR 7/4	5YR 6/6	5YR 6/6	5YR 6/3
J.C.	5Y 8/6	10R 4/4	10R 3/2	10R 3/1
B.O.	10YR 7/8	2.5YR 4/8	2.5YR 4/8	2.5YR 4/8
G.O.	10YR 7/8	2.5 YR 4/8	2.5 YR 4/8	2.5 YR 4/8
C.M.	10R 3/1	10R 3/1	10R 3/1	10R 3/1
R.E.O.	10R 3/6	10R 3/6	10R 3/4	10R 3/3
H.	10R 4/6	10R 4/6	10R 3/4	10R 3/1
mH	10R 2.5/1	10R 2.5/1	10R 2.5/1	10R 2.5/1
FeS_2	GLEY1 3/10Y	10R 3/3	10R 2.5/1	10R 2.5/1
FeSO	GLEY2 8/10BG	10R 4/8	10R 3/1	10R 2.5/1

3. Other natural pigments

Three other natural pigments were heat-treated in the same manner: English red ochre (N40351), powdered pigment-grade 'Hematite' (N48600) and 'Caput mortum' (N48720) (Kremer products). Via examination in the XRD, all three pigments were identified as hematite (33-0664). However, EDAX quantitative analysis revealed the presence of several other elements associated with the presence of phylosilicates (especially in the case of English red ochre; see Table 1).

Hematite and red ochre are significantly affected by the heat treatment: their color is gradually altered to deeper hues of red and, finally, they develop a purple-violet hue. Red ochre shows a tendency to slightly lighter hues in comparison to the hematite.

On the other hand, no color change is observed after firing of the caput mortum. Finally, no crystal structure modification is detected in the burned pigments, as they all retain the structure of hematite (33-0664) throughout the heat treatment.

It must be noted that the hematite grain size of the pigment is affected by the firing temperature: the higher the firing temperature, the larger the size of the hematite grains.

More specifically, it is noted that in case of the two red pigments (red english ochre and hematite), after firing at 700 °C grains which measure between 0.2 and 0.6 μm are formed, at 900 °C grains up to 0.9 μm and at 1100 °C grains with dimensions up to 3 μm. In the case of caput mortum the grains retained their initial size (1.3-6 μm) (see Table 3).

It was also noticed that upon grinding only the particle size of the pigment is affected (not the hematite grain size). More specifically, it was observed that after intensive grinding the mean particle size of the pigments was between 4 and 40 μm (Fig. 6).

Observation via SEM revealed that these particles (which size is modified via grinding) are composed of substantially smaller hematite grains (which size is affected by the firing temperature) (Fig. 6).

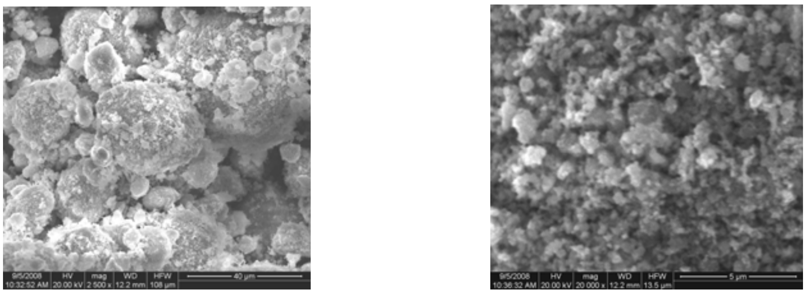

Fig. 6: Left: Particles in a natural hematite pigment after grinding; particle size: 4-40 μm (SEI, 2,500x). Right: hematite grains ('dust') on the surface of a paricle at the left picture; grain size: 0.1-0.4 μm (SEI, 20,000x).

Finally, as in case of the five yellow ochres, quenching of heated red ochre (H. and REO) in vinegar (according to the method suggested by Vitruvius, De Architectura, VII.XI.2)] did not affect their color.

4. Alternative iron sources

Three alternative iron sources (a: metallic hematite, b: pyrite and c: melanterite) identical (a,b) or closely related (c) to the natural ones accessible to ancient craftsmen, were also subjected to heat treatment. The three materials were identified via XRD and SEM (see Table 1) before firing, as well as after the three stages of the heat treatment. It was observed that in the cases of pyrite and iron sulfate the chemical composition and crystal structures were, as expected, affected by firing, as the precursors were converted to pure hematite. Further, new micromorphologies arose. The most notable of the features observed are as follows:

(1) Upon firing at 700 ^{o}C the plate-like morphology of pyrite is destroyed and hematite grains of ≈ 1μm diameter are formed (Fig. 7), while the pigment develops a dark red color. Firing at higher temperatures caused a slight enhancement of the hematite grain diameter and the pigment developed an even darker, violet-red color.

(2) Firing of iron sulfate to 700 ^{o}C led to hematite grain with a very small diameter (< 0.2μm) and the pigment exhibited a bright red color (Fig. 7).

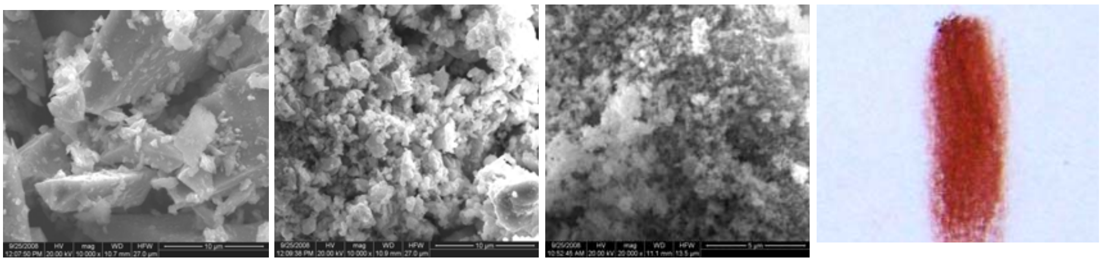

Fig. 7: Left to right: 1: initial morphology of pyrite (SEI, 10,000x), 2: hematite grains derived from the firing at 700 ^{o}C of pyrite (SEI, 10,000x), 3: hematite grains derived from the calcination of iron sulfate at 700 ^{o}C (SEI, 20,000x), 4: bright red color of the hematite formed after firing of iron sulfate at 700^{o}C

In the case of metallic hematite, the intensive grinding, to which the as-received mineral was subjected, resulted in the formation of a powder with deep red-violet color and hematite grains of 1-15 μm diameter (Appendix 1). No changes in the crystal structure and chemical composition and no substantial changes in grain size and color of the pigment were observed upon firing.

In Table 3, the main findings of the experimental approach are synopsized.

Table 3: Synopsis of the main experimental findings.

	Cr. Str./grain size	**Cr. Str.**/grain size	**Cr. Str.**/grain size	**Cr. Str.**/grain size
Sample	Initial	700°C	900°C	1100°C
1. OX2	**G**/-	**H**/0.2-0.5μm	**H**/0.4-1μm	**H**/1.1-3μm
2. OX3	**G**/-	**H**/0.2-0.5μm	**H**/0.4-1μm	**H**/1.1-3μm
3. OX4	**G**/-	**H**/0.2-0.5μm	**H**/0.4-1μm	**H**/1.1-3μm
4. R.E.O.	**H**/0.2-0.5μm	**H**/0.2-0.5μm	**H**/0.2-0.9μm	**H**/0.3-3μm
5. H.	**H**/0.1-0.4μm	**H**/0.2-0.5μm	**H**/0.4-0.9μm	**H**/0.5-3μm
6. C.M.	**H**/1.3-6μm	**H**/1.3-6μm	**H**/1.3-6μm	**H**/1.3-6μm
7. J.	**C, Q, K, G**/nd	**C, Q, H**/nd	**Q, H**/nd	**Q, H, A**/nd
8. F.O.	**G, K, M**/nd	**H, K, M**/nd	**H, M**/nd	**H**/nd
9. C.J.	**N, Q**/1-10μm	**H,Q**/0.3-1.3μm	**H,Q**/0.5-1.5μm	**H,Q**/0.5-3μm
10. B.O.	**Q, G, K, M**/nd	**Q, H, K**/nd	**Q, H**/nd	**Q, H**/nd
11. G.O.	**Q, G, K, M**/nd	**Q, M, H**/nd	**Q, M, H**/nd	**Q, H, A**/nd
12. $FeSO_4 7H_2O$	**F**/3-15μm	**H**/0.1-0.2μm	**H**/0.6-1.5μm	**H**/1-2.4μm
13. mH.	**H**/1-15μm	**H**/1-15μm	**H**/1-15μm	**H**/1-15μm
14. FeS_2	**FS**/1-20μm	**H**/0.3-1.5μm	**H**/1-5μm	**H**/1-10μm

Note: In the cases of Jarosite (J), French Ochre (F.O.), Burgunder Ochre (B.O.) and Gold Ochre (G.O.) no characteristic iron-containing grains were detected via SEM and the clay-dominated fine structure is retained throughout the experimental heat treatment.

DISCUSSION

A. The color of iron-oxide based pigments

It is well known that firing at temperatures above 275°C causes the transformation of goethite (α-FeOOH) to hematite (α-Fe_2O_3) (e.g. Sikalidis *et al*, 2006). This is the reason for the color change (from yellow to brown-red) observed at the artificial iron oxides upon firing at 700°C (Fig. 1).

Given that the furnace atmosphere remains oxidative during the treatment, no further changes either in chemistry or in crystal structure take place by heat treatment at higher temperatures (900-1100°C). Thus, the color changes induced by the raising of the firing temperature (700°C: red, 900°C: deep red, 1100°C: violet-purple) should be attributed to the increase of the hematite grain diameter.

Balek and Šubrt (1995) also refer to the growth of grain size upon increase of the firing temperature but they do not attempt a correlation between grain size and color. In addition, micro - morphologies similar to those observed in this study were detected during the heat treatment of artificial iron oxides by Legodi and de Waal (2007).

Although the latter authors note that color is affected by the firing temperature, they do not provide a clear correlation between firing temperature and pigment color.

Thus, the gradual color-change from brown-red to deep purple-violet is caused by the increase of the hematite grain size. Schwertmann and Cornell (1991) find that hematite crystals of 0.1 μm diameter are characterized by deep red color, while when their size is around 0.4 μm they develop a 'violet color'. According to our findings the ordinary (: non-deep) red color may be retained even when the size of the hematite grains is >0.2 μm, while the evolution of a deep violet hue necessitates a grain size in excess of approximately 1 μm. Finally, the unusually bright red color observed after calcination of iron sulfate at 700°C might be due to the unusually small size of the hematite grains (<150 nm; see Fig. 7). While no simple statements of sufficient generality as regards grain size and pigment color can be made (see pertinent section below) it is worth noting that in the case of hematite grains the gradual color (& hue) shifts with grain size are observed at sizes comparable to the wavelength range of visible light.

We have also found that all natural yellow ochres with high argillaceous content did not develop dark hues upon firing. The presence of argillaceous minerals affects significantly the color (Elias et al, 2006). More specifically, in the case of the above mentioned pigments, the fact that iron is present at relatively low concentration means that the hematite grains are dispersed in the clay matrix; thus, extensive sintering during firing is not possible and the formation of hematite grains having sufficient diameter for a further color change is prevented. Moreover, it is clearly observed that the micro-morphology of yellow ochres did not change significantly upon firing (Fig. 4). This is not the case for the yellow-colored 'Cyprian Jarosite': upon firing, the mineral natrojarosite disintegrates and hematite which forms is able to undergo grain size enhancement upon firing at higher temperatures. In addition, it was observed that although grinding affects partially the hue of the pigment, the most important factor for its color is the hematite grain size, which is enhanced with enhanced firing temperatures (unless largely trapped within argillaceous matrices).

The employment of electrolytic iron in this work aimed at excluding contributions to color changes from a variety of impurities, as it is often considered that manganese or other special impurities are necessary for the purplish tints of certain hematite-based materials; of course, this does not imply that special impurities can not affect the color of hematite-based materials.

Some key trends as regards color, processing, raw materials and grain size are presented in Table 4. Some of the same information is contained in the previous tables and the text in the Results section, while the rest derived from micrographs of all samples considered in this work. In order to make Table 4 a handy guide, colors are identified by their colloquial designation (as, after all, antiquity artisans chose colors on the basis of their perception and not on anything resembling a Munsel scale) and materials are identified by their actual character (rather than by their commercial designation). As regards the significance of designation on the basis of the iron-oxide content, see below.

2. *Significance of iron-oxide content*

It must be noted that the iron-oxide content of natural ochre-type yellow products can only serve as a coarse indicator of the capacity of the material to develop red or purple hues upon a given firing. This can be best understood upon consideration of an extreme material exception of artificial origin. Let us compare a natural ochre that remains dull yellow-grey upon 1100°C firing (as the [pseudo-]'Jarosite' of the present investigation) and an artificial mechanical mixture containing the same phases in the form of independent grains at the same proportions and subjected to an identical firing. Both materials will exhibit the same contents of iron-oxide and remaining phases. Yet upon firing the first material will be dull yellow-grey, while, according to our previous discussion, the second material will display a diluted red or diluted purple color, because in this case the hematite grains remain practically free to grow upon heating.

Table 4. Processing, grain size and pigment color
Part A (Table 4A)

	High iron yellow ochre	High iron red ochre	'Caput mortum'	Low iron Ochre ('Jarosite')	Artificial Ochres I	Artificial Ochre II
original	Yellow (goethite)	Red (hematite) 0.1-0.5μm	Purple (Hematite) 1.3-6 μm	Dull yellow	Flakes of variable sizes.	Flakes of variable sizes.
grinding	NA	NA	NA	NA	Yellow (goethite). Flakes and clusters of Needles	Yellow-brownish (goethite). Flakes/ clusters of Needles
700 ^{o}C	Yellowish red	Red (hematite) (0.2 to 0.5μm)	Purple (hematite) 1.3-6 μm	Dull yellow NDIOP	Red (hematite) 0.2 - 0.5 μm	Brownish red (hematite. 0.2 - 0.5 μm
900 ^{o}C	Reddish	Deep Red (hematite) (0.2-0.9μm)	Purple Hematite 1.3-6 μm	Dull yellow NDIOP	Deep red (hematite) (0.4 - 1 μm)	Deep red (hematite) (0.4-1 μm)
1100 ^{o}C	Reddish (slightly deeper hue)	Purplish (hematite) (0.3-3 μm)	Purple (hematite) 1.3-6 μm	Dull yellow NDIOP	Purple v(1.1 to 3^{+}μm)	Purple (hematite) (1.1 – 3^{+}μm)

Artificial Ochres I: derived from pure iron, or a steel, through the vinegar-metal route

Artificial Ochre II: derived from cast-iron, through the vinegar-metal route

Part B (Table 4 B)

	Metallic Hem	Melanterite	Pyrite	Natrojarosite
original	Bulk silver gray	Green 2-20μm ($FeSO_4 7H_2O$)	Gold-silver (pyrite)	Yellow (natorjarosite). Mostly 1 to 10μm
grinding	Purple (hematite), 1-15 μm	NA	Grey (pyrite), 1-20μm	NA
700^{o}C	Purple (hematite), 1-15μm	Bright red (hematite). 0.1-0.2 μm	Dark red (hematite), 0.3-1.5 μm	Red-violet (hematite), 0.3-1.3 μm
900^{o}C	Purple (jematite), 1-15μm	Red-violet (hematite) 0.6-1.5μm	Purple (hematite), 1-5μm.	Purple Mostly ca. 0.5-1.5 μm
1100^{o}C	Purple (hematite), 1-15μm	Purple (hematite) 1.0-2.4μm	Purple (hematite) 1-10 μm	Purple 0.5 to 3 μm

Grains below ca. 1μm always occur in clusters. Color might depend on the exact intracluster arrangement. Also, the grain size distribution will have an effect on precise hue. Main phases are identified when necessary (more phase details in previous tables). NA = Not applied, ND = Not determined, NDIOP = no distinct iron-oxide particles.

More generally, the 'iron-oxide content' criterion does not take into account: (a) the intimacy of mixing of the phases present, (b) the exact 'other phases' present, (c) the size of aluminosilicate platelets present (: larger platelets might be more effective hinderers of hematite restructuring/ grain coarsening). Hence, one cannot rely, at least fully safely, on iron-oxide content alone for an evaluation of color capacity changes upon firing, unless ochre-type natural products are relatively similar in various structural respects. Because of issues of this kind, Table 4 (or any other table listing the same type of, easy to consider, details as those of Table 4) is, strictly speaking, a report based on particular examples of each type of material referred to in the heads the columns. In brief, Table 4 is a handy guide but exceptions might occur. In addition, Table 4 does not cover contributions from potential chromophoric impurities.

3. Pigment color, grain size and its changes in a broader context.

In the 5th c. BC, Democritus [DK(Diels-Kranz)68, A135], in one of his trademark blends of glorious successes and glorious failures, suggested, possibly by combining his atomic theory views with inspiration from observations (on pigment and colored-stone powders etc) and certainly by adding fine intuition, that the colors are determined by the size, shape and arrangements of fine particulate matter. Democritus also stated that the more intense red color corresponds to larger atoms; if this is a statement based on observations and mental extrapolation to atoms, pertinent experience might derive from ground tinted (from the presence of impurities) stones (e.g. carnelian), which can be ground to colorless powders, rather than from the grinding of red & reddish pigments (see below). While most of the further details of the Democritus theory of colors bear no close relationship to reality and, also, the atomic scale arrangements need to be replaced by atomic arrangements at larger scales, the key Democritean claim about colors certainly recognizes some key contributors to the color of particulate matter.

The relation between pigment grain size and pigment color cannot be cast in sufficiently broad terms encompassing all pigments, except for the practical fact that the application of finer pigments is easier. Cennini, writing at around 1400 AD, emphasizes the benefits of near-endless grinding ('even for 10 years' for a version of yellow sandarac and 'even for 20 years' for artificial cinnabar in Ch. XLVIII and XL, respectively) but such statements can be best read as case-specific fanciful exaggerations; Cennini also suggests extensive grinding in the cases of hematite (Ch. XLII), realgar (Ch. XLVIII) and various other pigments. However, there are also clear cases where pigment size reduction through grinding quickly weakens pigment color and Cennini takes note of this possibility in the case of malachite (Ch. XLVII) and azurite (Ch. LX). More generally, the same grain size change, induced either by grinding or by other means (see below), can intensify (e.g. case of grinding artificial cinnabar), weaken (e.g. case of grinding malachite), mildly shift (see below) or radically change (e.g. cases of grinding metallic pyrite and metallic hematite) the color of a material. Further, the same extent of limited grinding applied to different materials of the same original grain size will lead, in general, to different final grain sizes. In addition, the color of applied pigments also depends on the relative refractive indices of the pigment and the medium (e.g. cross-linked linseed oil, inorganic glassy matrices etc) and also the color of the medium (if any), but this is only obliquely related to the present discussion, as long as, each time, our comparison pertains to various grain sizes of a single pigment.

Some attention should be given to the definition of grain size. For example, one must distinguish between grain size determinable by sieving, Stokes-terminal velocity and all other methods based on the dimensions of fully incoherent particulate entities [Gotoh et al., 1997] and grain size determinable by methods such as Scanning Electron Microscopy, where clusters consisting of finer grains can be resolved; as a matter of fact, grains under 1μm can never exist unclustered, at least in the dry state. Whatever the case-specific effect of grain size to the pigment color might be, the dimensions of ultimate grains (and, secondarily, their exact spatial arrangement) will be more important than that of free particles (that might or might not be clusters of smaller grains). Mild shift of color based on grain size alone was documented in the present work in the case of fine pigments with a hematite phase. We have found that hematite grains larger that ca. 1 micron (regardless of the method of generation, e.g. through grinding of bulk mineral or through size enhancement via heating of submicron products) exhibit a purplish color, while those under 1 micron are deep-red and bright-red at ca. 0.5 microns. Crossing of the 1 micron border (specific to the color of hematite) by reducing grain size through grinding appears to be difficult in view of the capacities of the mortar-and-pestle processing (see below) though a color-modifying, submicron tail of the size distribution is possible; overall, relatively fine hematite pigments (a particle size distribution peaking at around 10 μm or lower) are not expected to exhibit significant color shifts upon grinding.

The effect of mortar-and-pestle grinding usually has a lower particle size limit in the range of 1 to 5 microns; yet, this limit appears to pertain more to the dimensions of free particles (not to the hematite grain size). In any case, grinding is not the only simple means of producing pigments of reduced grain size. For example, pigments produced by chemical modification of raw materials (especially those produced by decomposition, as in the case of heated melanterite considered herein) might well consist of cracked-down, in terms of size, versions of the precursor particles. Also, properly-controlled precipitation from solution can lead to fine grains, though we do not have clear antiquity examples of the application of this concept, except for the case of certain glasses (precipitation of Cu and Cu_2O fine grains in antiquity red glasses); yet, the latter situation is related to the precipitation from solution only from the modern point of view of glasses. No general statement can be made as regards the particle size obtainable by corrosion (as, for example, in the case of the metal-vinegar route); it is only that iron tends to corrode via formation of porous and fragile oxidation products and, hence, even limited grinding of the corrosion products might lead to fine particulate morphologies.

As regards grain size enhancement (in the absence of a compositional change), the simplest appropriate route is via heating, which can lead, through a variety of material species redistribution processes (capillary, diffusional etc), to the size change in consideration. Higher temperatures and longer heating periods lead to larger grain sizes. Finally, the case of size enhancement effectively obstructed by the surrounding platelet-like phase(s) deserves attention. As shown in the present work, the immobile platelet-dominated aluminosilicate matrix served as a set of obstacles geometrically preventing redistribution of iron-oxide species to fewer and larger particles, thus making low iron-oxide ochres inappropriate as raw materials for red or darker hematite pigments.

4. Antiquity practices and potential practices as regards pigments based on iron (III)-oxide

Antiquity references to the practices leading to red or darker iron (III)-oxide pigments as well as representative references to the metal-vinegar route applied to Pb, Cu and Ag have been presented in the Introduction of this work. Accompanying considerations and data presented in previous sections suggest that a range of handy iron-based raw materials much broader than natural yellow and red ochres was available and used, at least occasionally, in parallel to the natural ochre products for pigment purposes. If nothing else, the, rather improbable on intuitive grounds, reference of Dioscurides to the firing (and, hence, destruction) of an impressive mineral such as magnetite and the accidental (: located in a book dealing with metals) reference of Theophilus to the firing of melanterite might be thought of as lucky instances of allowed access to the antiquity knowledge and practices of alternative routes to iron-oxide pigments. As regards the iron-vinegar route, unless some, non-obvious to us, convincing counter-argument can be presented, it appears practically impossible that this option was systematically bypassed during antiquity, despite its obvious character, ease of application and clear benefits: (a) low cost, (b) wide possible color range of products, (c) independence from the availability of a range of high quality natural ochres. It might simply be that as 'ios khalkou' could designate verdigris, the frequently mentioned 'ios sidērou' would designate not only the naturally formed rust on iron objects but also, occasionally, the better controlled and quickly obtainable pigment products through the iron-vinegar route.

Among material preparations presented herein and compatible with antiquity capacities we wish to highlight the following:

(a) The iron (or steel)/vinegar route (plus firings) is a low cost (e.g. applicable to cleaned metal scrap) and quite versatile (as regards the range of potential colors) method of producing iron-oxide based pigments.

(b) One of the simplest ways of producing a purple pigment based on iron-oxide is the intense grinding of metallic hematite; grain size remains largely above 1 μm and, hence, no firing is necessary. This is a labor-intensive method, yet one requiring minimal only equipment.

(c) A bright red iron oxide pigment can be formed by thermal decomposition of melanterite to a material with a 0.2-μm fine structure.

Finally, we were incapable of duplicating the 'vinegar quench of hot ochres' method of purple pigment production referred to by Vitruvius. It might be that the Vitruvius report is a garbled account of a more complicated processing; the similar report by Pliny (see Introduction) does not necessarily add weight to the testimony of Vitruvius, as Pliny is largely a compiler of information found in earlier sources. It is also possible that a purple color can develop via vinegar quenching but only as a result of sorption of appropriate impurities, either from vessels or from certain organic substances (e.g. tannins) contained in some vinegars. Alternatively, the change to purple might be possible for special ochres, substantially different (with regards to some crucial and undetermined feature) from those tested by us. The only thing that can be stated with certainty is that the route to iron-oxide based purple described by Vitruvius is not a guaranteed one.

The way to differentiate iron-oxide based antiquity pigments by the routes considered here from those usually considered in the literature will require extensive future work that will involve the development of micromorphological, fine-compositional and spectroscopy-based criteria and subsequent comparisons with antiquity samples. Visual comparisons will save some time but will not take us far enough safely enough; if nothing else, this work documents that it was easy to produce during antiquity iron-oxide based pigments which did not rely on ochre raw materials but *look* very much like iron-oxide based pigments having ochres as raw materials.

CONCLUSIONS

During the experimental investigation of the production of artificial iron oxides via calcination of natural, artificial and alternative iron sources, it was shown that by using more or less standard procedures it is possible to produce a variety of hues between red and purple/violet. The color can be affected by the final hematite grain size alone, but this is determined by a combination of factors: initial grain size, temperature and duration of firing, and the level of microstructural obstacles (such as aluminosilicate platelets) capable of hindering grain growth. All materials employed as well as the furnace temperatures employed were accessible to the ancient craftsmen.

Electrolytic iron and other, essentially free of impurities, iron oxide precursors indicate that no particular impurities (such as manganese etc) are necessary for the development of pigments based on a hematite phase with a purple/violet color. In the case of natural iron oxide products that contain high loads of aluminosilicates, the latter hinder the formation of large hematite grains. Thus in most cases natural yellow ochres cannot alter, upon firing, their color beyond red (i.e. to purple/violet) and it is even possible that the color can remain, despite strong firing, close to yellow. In addition, quenching of the hot iron-oxide pigments in vinegar did not affect significantly their color; the pertinent Vitruvius recipe is either garbled or an insufficiently general one. The grinding of metallic hematite offers a purple pigment without the need of a firing step. The metal/vinegar approach, with metal = iron or steel, explored herein constitutes an obvious, low-cost and versatile route to earthy iron-based pigments, and, despite the lack of pertinent records, it is hardly believable that it was systematically bypassed during GraecoRoman antiquity. Finally, an attractive intense red can be obtained by firing ‘melantēria’ and, again, a GraecoRoman antiquity application is considered possible.

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APPENDIX 1: REFLECTION SPECTRA OF SELECTED PIGMENTS

The evolution of color upon processing is traced herein through pigment reflection spectra in the visible region. The data pertain to three key processes described in the main text. All spectra were collected using a GretagMacbeth SpectroEye spectrophotometer.

I. Color evolution upon firing of artificial iron oxide (vinegar route)

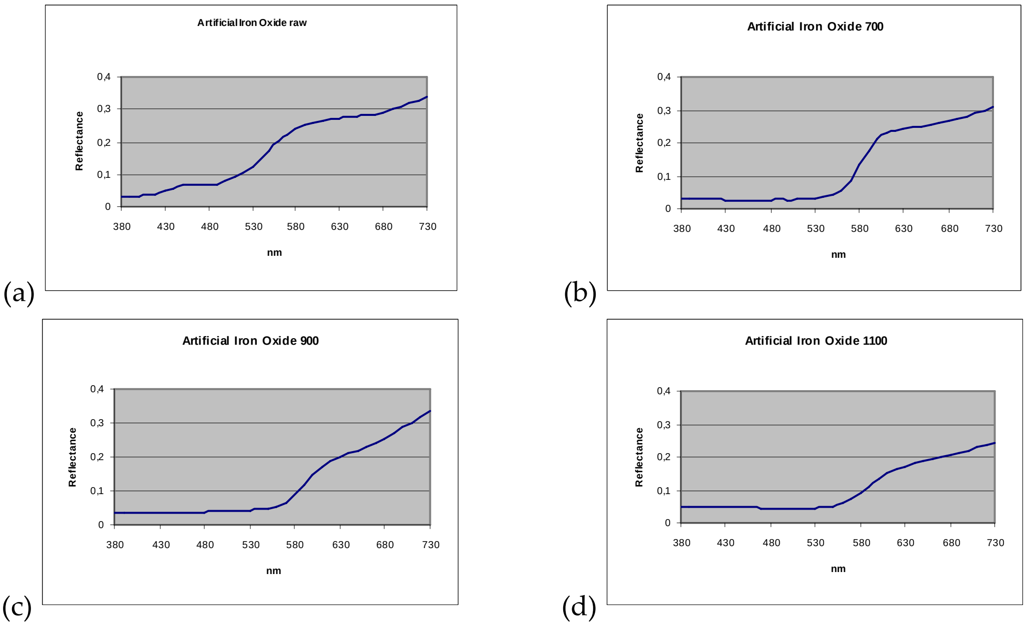


Figure 1: Visible spectra of artificial iron oxide. From top left to bottom right: a: initial product (vinegar route), b: product of firing at 700°C, c: product of firing at 900°C, d: product of firing at 1100°C.

The initial brown-yellow color of the artificial iron oxide (a)) shifts towards red upon firing. The product of the firing at 700 °C (b) presents significantly lower reflection in the green-yellow region (530-590 nm) which is further decreased upon firing at higher temperatures (900 and 1100 °C, c and d respectively) and, thus, red color prevails. Red color becomes darker upon 1100 °C firing (see text-table 2) as a result of reduced reflectance (d).

II. Production of deep red color by metallic hematite grinding

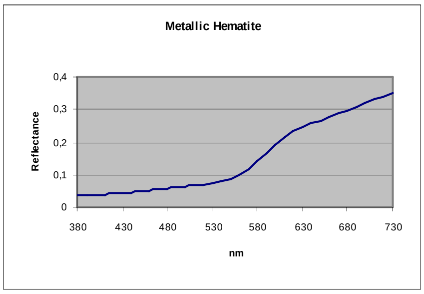
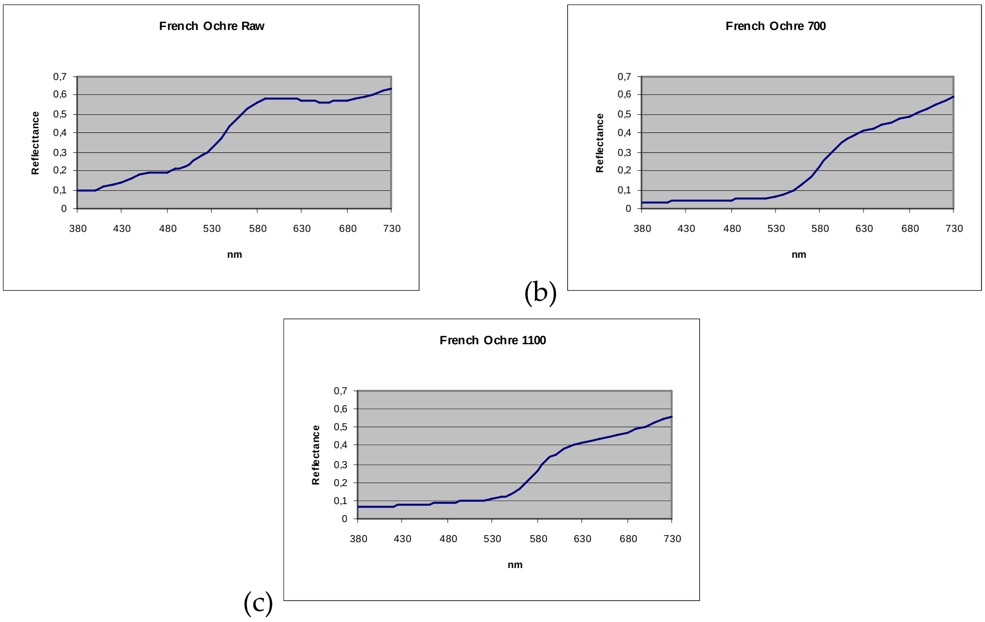


Figure 2: Visible spectrum of grinded metallic hematite

In figure 2, the spectrum of visible reflection of grinded metallic hematite is presented. It is obvious that by simply grinding hematite, a deepred pigment is obtained with no need for further heat treatment. Its spectrum is almost identical with that of the product of 900°C firing of artificial iron oxide (see Figure 2, c).

III. Product of natural yellow ochre firing



(a)

(b)

(c)

Figure 3: Visible spectra of natural yellow ochre ("French Ochre") and its products. a: the as received yellow pigment, b: product of firing at 700°C, c: product of firing at 1100°C

The bright yellow color of natural ochre (high reflectance at the region of 550-580 nm-a) is affected by firing at 700°C: the pigment gains a bright (high reflectivity) reddish hue (b). Only minor changes are observed upon further firing at higher temperatures (c)