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Clay and iron oxide pigments in the history of painting

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Abstract

Clay minerals and iron oxides are intimately related in the process of their natural formation. Their mineralogical composition and physical properties correspond to the physical–chemical conditions of weathering, sedimentation and alteration processes by means of which these minerals are associated giving different types of laterites, ferrolites, ochres, and coloured clays and soils. Very early in human history, these and other clay materials were adopted as mineral pigments. Their structural and mineralogical features are directly related with their natural genesis and provenance and help us in the study of historical painting techniques and materials. This paper gives general information about geological sources and their characteristics, the literary evidence of use of different forms of earthy pigments on historical paintings, about analytical methods suitable in their identification within the ground and colour layers of the painting, and handling with the samples of works of art. The examples focused preferentially on the period of European mediaeval and baroque painting.
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1. General outlines and terms

The fine arts and natural sciences are apparently different domains with different tasks, tools and schemes. The art of painting is a kind of the creative activity, where attenuate human ideas and visions are expressed fairly materialistically, through colour. Colour can be taken either as a sensual perception or as a physical phenomenon. But undoubtedly, colour is directly related to the chemical and structural character of the material; therefore the same question, e.g. 'Why it looks greenish?' implies totally different

sense for historical and natural scientists. Historians look for symbolism of colours and thought reasons that led the painter to use a specific material at a given context. Natural scientists look for the origin of colours in the material that reflects the process of its natural genesis and/or artificial origin. Colour (painting) layer, which is the basic building element of painting, is a mixture of materials—pigments and binding media; their composition gives the colour quality. The main aspects of this quality—colour stability and hiding power—can be strongly time-dependent due to the interactions of chemical species within the mixture and with surrounding environment. In the process of restoration of historical paintings, some colour changes can be designedly preserved as a typical result of aging patinas. In the cross-section view, painting layers appear in sequences correspond-

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ing to the periodic technological principles, the authors' invention and a presence of latter re-paints.

In the Old European paintings, the technological principles were held relatively strictly. The colour sequence starts with ground layers that served as a coating material to prepare the surface of a panel or canvas and were also closely related to the techniques and materials in the subsequent painting. The painting sequence is usually finished by varnish mainly based on natural oils and resins. In the European fine arts, one of the first famous manuals of technical experiences, material preparations and painting itself, is the early renaissance work by Cennino Cennini issued first in 1437 (Cennino, 1978). A very good review of treatises and 'recipe-books' from the 12th to the 18th centuries is given by Merrifield (1967). Then, further works on painting techniques with a general scope should be mentioned, e.g. Eastlake (1960), Laurie (1967), Berger (1973) or, in the Czech literature, Slánský (1953, 1956).

Pigments of colour layer are either natural (mineral) applied simply after mere mechanical pre-treatment and separation not-affecting their chemical or phase composition, or manufactured (synthetic) prepared by chemical reactions from substantially different raw materials. In a relatively lower extent, also organic pigments are prepared from organic dyes by precipitation on inorganic substrate. Fundamental works on pigment origin, preparation, use and identification are given, e.g. by Harley (1982), Feller (1986), Roy (1993) and Fitzhugh (1997). In these general works, earthy pigments, representing a great group of clay-rich materials used in the fine arts, are not satisfactorily described with respect to their mineralogical and structural variability and origin, possibly due to the complexity of the microanalysis of clay materials. Mineralogical approach in the study of natural pigments is necessary, when detailed information on the origin and preparation procedure is needed; provenance of the material and, in an interdisciplinary field, the provenance of the artistic work is to be discussed.

2. Earthy pigments

In a widely used art and conservation terminology, earthy pigments are distinguished on the basis of colour as yellow ochres, red earths and boles, green earths, dark yellow or brown siennas and umbers. The use of white earth, represented predominantly by China clay (i.e., high grade kaolin), is limited in the pictorial art in Europe. Sometimes it occurs as an inert pigment or extender (e.g., Huxtable and Pickering, 1979) or, because of its clarity and high absorbency, as a base for certain lakes (Mayer, 1991). In much wider extent, kaolin is applied in the paper industry (Beazley, 1991) and from the ancient times also in porcelain and ceramic bodies (Yanyi, 1987) or as an inert wall coating.

Konta (1995) wrote that the earthy pigments might be divided according to their colouring agent: it is either some non-clay pigment, e.g. iron oxides, or a chromogenous element in the clay structure. Majority of earthy pigments belong to the former group, while green earths belong to the latter group, because in most cases their colour is given by the specific ratio of divalent and trivalent iron in the structure of minerals glauconite, celadonite, or locally used smectites and chlorites, with the hue possibly altered by minor goethite admixtures. Historical sources of these minerals are well known and described in literature in general, but in real observations on historical fragments, it is very difficult to distinguish among mineral forms.

3. Clay pigments

3.1. White earth

Within the pictorial art, the historical use of white earth is located predominantly in Asia; in Japan, white clay pigments commonly appear up to 15th or 16th century before they are displaced by a calcium carbonate white made from pulverized oyster shells (Winter, 1981). They are documented as kaolinite-rich kaolins used in grounds (= surface coating materials), with some variation of composition, perhaps corresponding to their geographical origin. Typically, kaolin-type clays are used as priming coats in *in secco* wall paintings applied directly on a plaster in Japan (Akyiama, 1985), China and India (e.g., Agrawal and Jain, 1984) and as grounds of Buddhistic wooden sculptures (Yamasaki and Nishikawa, 1970). In the orbit of orthodoxy (Russia, Bulgaria, etc.), white clay

priming coats are found in a plenty of icons. It makes difficulties to specify the source locality of kaolinite-rich clays used in artistic works even if mineralogical investigation is possible. As reported by Souaya et al. (1983) chemical and mineralogical testing of nine white clays from various sites used in pictorial art of ancient Egypt surprisingly showed a lack of a correlation between their composition and geological age of the weathering/deposition.

In the European cultural history, the application of grounds (beneath tempera paints) replaced the ancient Greek encaustic technique (i.e., direct hot wax colours application on the wood) in the period of subapostolic icon art (Bentschev and Hanstein-Bartsch, 1997). In Middle Ages in Europe, grounds applied on wood panel surfaces are already very common, but they are mostly made from white chalk or eventually gypsum (called *gesso*) in the Italian fine arts. Clay minerals can partly occur in the grey priming layer appearing sometimes on the base of chalk grounds, e.g. in Mid-European wooden panel paintings and sculptures of 14th century, and referenced as probably a clay-rich chalk (silt) pigmented by natural bitumens or graphite. As we have found earlier (Hradil et al., 2002), in agreement with experience of Hamsík and Tomek (1983, 1984), this grey chalk is mixed only with quartz and the content of clays is relatively very low. Clay-rich grounds started to replace chalk and *gesso* in paintings of 16th century and, generally, they are predominant in the 17th and 18th centuries (in Baroque) in all European countries. These red-orange grounds are most probably clayey ochres but, occasionally, can be prepared mechanically by mixing of materials of different origin, where white kaolinite is used as an extender. The question of a different or common origin of clay minerals and iron oxides in ochres is relatively old and discussed in some cases also in the field of archaeology; e.g., Judson (1959) suggested that white clay—kaolinite—found in late paleolithic excavations was used as an extender pigment in a mixture with hematite.

White clay extenders mainly occur as an alternative to alumina, alums or baryte in the process of organic pigments preparation. One unique example is given in the case of Maya blue, a pigment used by Mayas in Yucatan already in the 8th century. As described by Van Olphen (1966), the pigment is remarkably stable: its colour is not destroyed by hot concentrated mineral acids or by heating to about 250 °C. Its composition and structural features had not been found until the synthetic analogue was prepared in the second half of 20th century. It is proposed that the pigment is an adsorption complex of attapulgite and natural extract of indigo plant, which is oxidised on the surfaces of the clay particles. As reported by many authors, e.g. Van Olphen (1966), Littmann (1980, 1982) and others, this complex should be heated for a long time at a temperature of about 100 °C to reach the stability described above. Kleber et al. (1967) described that even higher temperature between 150 and 200 °C is necessary to markedly improve the pigment resistance because of the irreversible substitution of the zeolitic water by indigo molecules. Latest studies (e.g., José-Yacamán et al., 1996) focus the detail determination of the nanostructure and crystallochemistry of the complex using high-resolution transmission electron microscopy and other modern methods. Experiments proved that also other zeolite-like clay minerals such as sepiolite could form similarly stable complexes. One of many varieties of Maya blue is supposed to be only pure bluish montmorillonite without admixtures. Similar rare case was described by Casas and de Andrés (1992) on Romanesque wall paintings in Catalonia and Andorra, where blue zeolite mineral aerinite has been identified; its name comes from Greek 'aerinos' = colour of blue sky.

When an industrial production of pigments quickly developed in 18th century, the number of white extenders was further increased. A typical example is the production of Prussian blue, which can be supplied pure-colloidal, but also extended by alum, baryte, iron oxide, alumina, calcite, gypsum or white clay (Fig. 1). Mixtures with extenders are usually differently denominated, e.g. as Antwerp or Brunswick blue. Berrie (1997) summarised that the white earths coloured either by indigo or Prussian blue are also known in the literature as 'mineral blues'. The clay extenders (kaolin, talc) retain their importance until the present time (Lawrence, 1960).

3.2. Green earth

The terminology, properties and history of the use of pigments generally known as green earth are described in detail by Grissom (1986). Different silicate materials of dull greyish green colour are
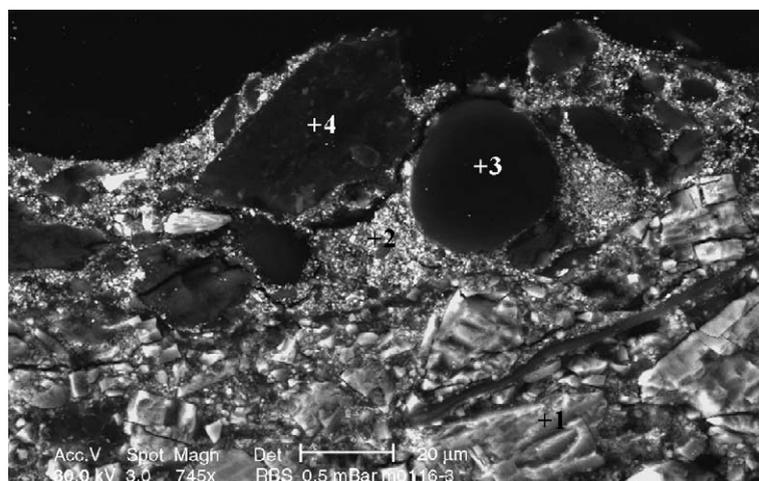
Fig. 1. Morphological evidence for the use of inorganic extenders in the painting layer; 'The Virgin Mary Protectress' gothic wooden panel painting of the unknown painter (National Gallery in Prague). Repainted at 1816. The upper unoriginal layers of coarse grinded barite (+ 1) and artificial fine-grained white lead (+ 2) are pigmented by blues of different origin—colloidal plant indigo (+ 3) and Prussian blue fixed on the angular grains of alum extender (+ 4). (Obtained by SEM PHILIPS XL 30 CP electron microscope in the constant pressure regime with Robinson detector of backscattered electrons, working voltage 30 kV. Photo: Snejana Bakardjieva.)

widely found throughout the world, but the very green earth is prepared principally from two closely related clay minerals, celadonite and glauconite. Although their crystallochemical differences and classification are subjects of discussion, celadonite is traditionally considered a magnesium-rich and glauconite an iron-rich dioctahedral clay micas. The distribution of divalent and trivalent iron in the structure, which results in their green colour, is studied by numerous methods (Drits et al., 1997). They are generally thought to be of a different origin. Celadonite occurs in small quantities as a relatively pure substance in vesicular cavities (amygdules) or fractures in volcanic rocks, associated with zeolites. Glauconite, less pure but more widely distributed, is often found in the form of small greenish pellets in sedimentary rocks of marine origin (= green sand). With respect to the source locality, even other clay minerals can be incorporated into pigments labelled as green earths, e.g. montmorillonites, chlorites, and kaolinites. Admixtures of free ferric oxides such as yellow goethite are also common.

Qualitative differences among natural sources have long been recognised since ancient times—according to source texts of Vitruvius and Pliny (e.g., Vitruvius, 1993) they were located in Smyrna of Asia Minor or Cyrene (now Ain Shalat-Greena) in Libya. Green

earth is widely documented in Roman wall paintings (e.g., Augusti, 1967; Delamare, 1987; Delamare et al., 1990; Béarat, 1996, 1997; Wallert and Elston, 1997), ancient Byzantium (Gettens and Stout, 1958) and also in Japan (Yamasaki and Emoto, 1979). Glauconites or celadonites are usually identified; their sources in Gallic green phyllites from the Roman period are mentioned (Odin and Delamare, 1986). In many cases, a mineral name is missing. Chlorite is also occasionally mentioned in samples from Switzerland, France and Pompeii, source localities of celadonite in Northern Italy and Cyprus are widely discussed in the literature. In contrast, green earth has only rarely been found in Cretan fresco painting, where mixed greens made from Egyptian blue (copper silicate) and yellow ochres were identified (Neuberger, 2002) and in ancient Egypt, where different copper greens widely predominated (Lucas and Harris, 1999; Colinart et al., 1996).

The best-known use of green earth is the under-painting of flesh in mediaeval easel painting in Europe. The tradition of employing greenish mixtures in rendering flesh is recorded in texts from 11th to 15th centuries, e.g. in the oldest Mt. Athos manuscript (Schäfer, 1855) or the famous Cennino Cennini trea-tise (Cennino, 1978). Green earth was also used as the ground for gilding in mediaeval painting known as

'green bole'. In oil, green earth is alternated by copper greens; it is the reason of its absence in early Dutch paintings and its slow disappearance after the Renaissance. Green earth did not cease entirely. On the continent, in contrast to England, the pigment is used extensively throughout the 17th, 18th and 19th centuries as it is documented in many works of art.

As an example, discrete grains of green earth are clearly visible in the colour layer of the 'sea' in the famous painting of Ch.A. Coypel (1694–1752): 'Armida is watching the destruction of her palace' from the Gallery of Fine Arts in Ostrava (Hradil et al., 2002). Their shape, dark colour, relatively high content of magnesium and possible admixture of zeolites found by infrared spectroscopy could indicate celadonite rather than glauconite (Table 1). As the most famous source locality of celadonite in baroque Europe, the deposit Monte Baldo near Verona in Northern Italy is widely mentioned in literature, firstly in 1574 (De Brignoli de Brunnhoff, 1820). 'Verona earth' of high chroma and bluish green colour is still considered as the best variety, but many other sources are noted in 19th and 20th centuries, e.g. in Bohemia, Saxony, Tirol, Poland, and Cyprus (Grissom, 1986).

Distinguishing between celadonite and glauconite in works of art is quite difficult; it is mostly indirect and questionable, as powder X-ray diffraction is insufficient. Alternative analytical methods are hence used such as infrared and Mössbauer spectroscopy (Dainyak and Drits, 1987; Drits et al., 1997; Casellato et al., 2000). Identification of other green minerals is much easier and is documented in rare examples, e.g. in the finding of septochlorite mineral cronstedtite in the Bardwell portrait of William Crowe in England (Mosk, 1975). These occurrences are related to the source localities of only a local importance, e.g. the chlorite deposits in English Cornwall or greenish bentonites in Nothern Bohemia.

4. Iron oxide pigments

4.1. Yellow and brown ochres

Earthy pigments varying from dull yellow to red and brown are commonly called ochres in the economic geology, mining industry, and painting. Ochres are defined by Mayer (1991) as clays used to make the earth colours; in pigment terminology, the word ochre is predominantly used as a synonym for yellow ochre. Its colour is given by a presence of different iron oxyhydroxides and oxides, mainly goethite and hematite; sometimes the colour is brownish due to manganese oxides. Different shades occur in many surface deposits and are hence relatively cheap and easily available. Their use as artistic pigments has started in pre-historic times and quickly became very common in all over world. They are found in paintings of each region and historical period; therefore, it is afield to refer about particular cases. Because of very long history of use, ochres are considered as unsuitable for dating of paintings and searching for their provenance; their mineralogical variability in relation to possible natural genesis remains hence unrecognised in practice. In the 19th century, during intensive development of the chemical industry, synthetic iron oxides—the so-called Mars colours—are introduced to painting. However, natural ochres have in fact never been fully replaced because of their availability in nature; in many recent cases of pigment preparation, native clay-rich materials are mechanically mixed with synthetic iron-based pigments. Recognition of a method of preparation is difficult when operating with minute historical fragments and therefore the indication of ochres instead of Mars colours is very common in practice (Harley, 1982). Factors indicating the provenance of ochres can be found in their mineralogical composition, particle size and crystal quality.

Table 1
Comparison of mean crystallochemical composition of green earth minerals (hydrogen and oxygen are excluded) with the single grain EDX microanalysis within the real painting layer

Element	Glauconite (wt.%) mean values	Celadonite (wt.%) mean values	Green earth from the Coypel's painting[a] (wt.%)
K	10.1	16.6	16.7
Na	0.5	–	–
Mg	4.2	8.3	6.7
Al	3.5	1.2	4.2
Fe	36.0	26.1	22.0
Si	45.8	47.8	50.2
Fe/Mg ratio	8.6	3.2	3.3

[a] Green earth from the painting of Ch. A. Coypel (1694–1752) 'Armida is watching the destruction of her palace' has been interpreted as aluminium-rich celadonite.

In pre-historic times, the natural sources of ochres are generally unspecific because of the plenty of places with local importance and high mineralogical variability. In Europe, the use of mineral pigments has started in the Paleolith (Meszaros and Vertes, 1955). Rock paints are the most spectacular in the epoch of Magdalénian with the famous evidences in the rock caves of Lascaux (Dordogne, France), Niaux (Ariège, France) and Altamira (Santander, Spain) (Couraud, 1987; Vouve, 1995).

In painting of later historical periods, higher finicality about pigments is expectable when the international market with products from selected localities has developed. Unfortunately, there is an insufficient set of evidence for it; the mineralogy of earthy pigments found in historical paintings is not satisfactorily described. In old literature, the place of origin was sometimes incorporated in the name of ochre; dull yellow 'spruce oker' may be taken as an example— 'spruce' being an old form of Prussia (Academia Italica, 1666). The particularly transparent variety of ochre found near Siena in Tuscany, Italy, was initially described as 'Terra di Sienna'. In the 19th century,

that term was anglicised and abbreviated to general forms 'raw (or burnt) sienna' without relation to the pigments provenance (Harley, 1982). A less-known case of such shift from a locality–related name to a general type mark is 'Armenian bole', which was later used for any clayey red of certain technological properties. High mineralogical variability can be demonstrated when recent commercial analogues of natural earths are compared. Clay-rich French ochres pigmented by goethite always contain well-ordered kaolinite and some illite, Italian ochres from Tuscany are always rich in gypsum (the 'gesso' type) sometimes accompanied by expandable clay minerals (Fig. 2). In localities with higher activity of sulphur (volcanic areas, pyrite-rich outcrops), iron sulphates can also be found (e.g., jarosite); furthermore, such pigments are denoted as ochre.

The joint occurrence of Fe oxides and kaolinite in continental sediments is understandable not only due to their simultaneous formation, but also due to similarity in their particle size and aggregation by Coulombic forces (clay minerals and Fe oxides differ in points of zero charge, Cornell and Schwertmann,
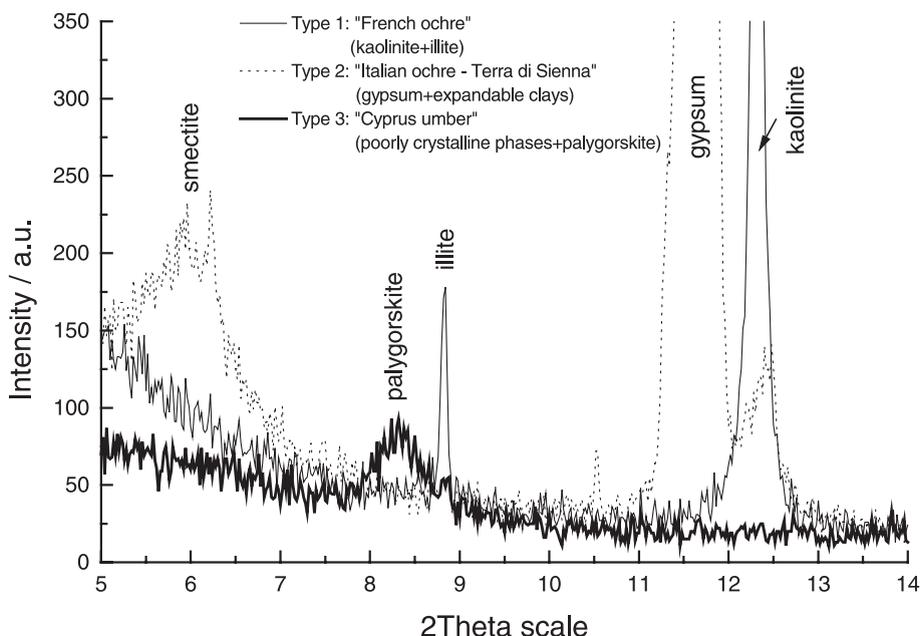

Fig. 2. Clay minerals in three main types of native ochres from recent commercial production—a detail of the beginning of XRD pattern. French and Italian ochres are both accompanied by only a few percents of goethite, whereas in the Cyprus umber the goethite is dominant as a massive limonite. (Obtained by SIEMENS D-5005 difractograph, CuKα radiation, secondary monochromator, range $3-80°$ 2θ, step $0.02°$ per 8 s.)

1996). Kaolinic goethites, e.g. of a weathering mantle formed in Europe in pre-Cretaceous, have traditionally been used as yellow earths. 'French ochre' mentioned above can serve as an example: it is still mined and mechanically refined, e.g. in Provence, France (Onoratini and Perinet, 1985). Similar local sources in other European countries have been used as natural ochres until 20th century.

Although Fe oxides are extremely abundant on the Earth surface (Cornell and Schwertmann, 1996), so far not one of such oxides is suitable for pigment use. For example, recent ochreous (brownish) precipitates formed in surface waters rich in Fe^{2+} (weathering of pyrite followed by fast abiotic oxidation of Fe^{2+}) are composed of poorly crystalline Fe oxides, including amorphous phases and ferrihydrite (Singh et al., 1999). Similarly, Fe oxides formed in recent soils in temperate climate consist of less crystalline phases due to a presence of inhibitors of crystallization, especially silica species and organic matter. Pedogenic goethite and hematite have specific surface areas, in orders of 100 m^2/g (Cornell and Schwertmann, 1996), and hence their colour strength is insufficient.

The hue of goethite is affected by its crystallinity and elemental purity. Finely particulate (poorly crystalline) goethite, commonly called limonite in the past, is brownish yellow. Because the colour strength of hematite is greater than that of goethite, as low as a few percent of hematite admixtures change the hue of goethitic yellow earths to brownish or reddish. Mn-for-Fe substitution turns the goethite colour to olive-greenish or greyish (Cornell and Schwertmann, 1996): this probably also contributes to a brown hue of raw umbers, which can additionally contain dark Mn(III,IV) oxides. Well-crystalline bright yellow goethite of outstanding pigment properties consists of particles with specific surface area of several tens of m^2/g (units m^2/g for synthetic analogues).

Goethite only uniquely occurs in nature in a pure form or as a massive mineral. Goethite or goethite/hematite mixtures free of clay minerals can be formed by oxidation of pyrite that is probably the major case of brownish limonites. Well-crystalline particulate goethite is formed, e.g. by intense chemical weathering of basic or neutral rocks in humid climate, especially in thick weathering mantles such as deep lateritic profiles, and is hence commonly accompanied by kaolinite or gibbsite. High activity of water is a necessary prerequisite enhancing goethite/hematite ratio in the weathering products. A typical example of goethite parent minerals is olivine, which is weathered topotactically to a mixture of smectite or kaolinite and goethite (Cornell and Schwertmann, 1996). Augite, biotite and hornblende are other sources of Fe sufficient to form well-crystalline goethite (Allen and Hajek, 1989, Cornell and Schwertmann, 1996).

Earths of darker colours are usually called siennas and umbers: they can contain admixtures of hematite and Mn(III,IV) oxides. Following historical literary evidence, umber is named after the source locality in the district of Umbria in Italy (Bardwell, 1795), or, according to the French writer Watin (1772), its name is derived from the Latin 'ombra', which means 'shadow'. It corresponds to later documentary sources, where umber is described as being very suitable for shadows or for shading other colours (Harley, 1982). Umber was imported mainly from Turkey; its best bluish variety comes from Cyprus, which have been classed as part of Turkey in the 18th century. Cyprus umbers are still available. They are closely related with the weathering of Troodos ophiolite complex of obducted oceanic crust. Associated with radiolarites, they cover the upper parts of the profile with Troodos pillow lavas and massive Cu−Fe sulphide ores. These massive goethite-rich umbers contain amorphous Mn(III,IV) oxides and can be accompanied by palygorskite (Fig. 2) (Grygar et al., in press).

The provenance of ochres is difficult to recognise, although the accompanying minerals are of definite diagnostic value (presence of calcium sulphate, presence and crystallinity of kaolinite, the content of expandable clay minerals). Beside the mineralogical analysis, the isotopic measurements known in the sedimentology can be very helpful. The method is based on the premise that the stable isotope ratio, e.g. $^{18}O/^{16}O$ in the quartz grains of sediments, accurately records that of their parent rock types and are resistant to alteration and isotopic exchange in low-temperature environments; therefore it can be used to characterise different rock types participating on the genesis of studied sediment; the method has been used, e.g. in the study of Australian archaeological ochres (Smith, 1997).

The natural ochres as well as brown siennas and umbers have traditionally been calcined to obtain

reds; this technique was likely known as early as Paleolith (Helwig, 1997). Hematite so formed by goethite dehydration can be revealed by XRD specific line broadening due to residual structural OH^- or cation disorder (Perinet and Onoratini, 1987; Helwig, 1997; Pomies et al., 1998, 1999) and by dehydration pores apparent in TEM micrographs (Pomies et al., 1999). These effects assume that the temperature of calcination was well below 800 °C, when re-crystallization by solid-state diffusion would heal both these defects. In particular, dehydration pores are highly specific morphological features of hematite formed by relatively low-temperature calcination (Cornell and Schwertmann, 1996).

4.2. Red earths and boles

Natural reds are of a different provenance (e.g., Persian Red, Spanish Red), but their colour is always given by the presence of hematite. In contrast to goethite, hematite is not formed by topotactic reactions during chemical weathering, and so hematite relation to clay minerals is not so straightforward as in the case of goethite. Nevertheless, red clays are very common in nature, probably also due to the physical association of Fe_2O_3 and clays. Well-crystalline hematite of about a micrometer crystal size has a distinct violet tint differing from the bright red colour of, e.g. pedogenic, hematite with sub-micrometer particles. On the earth surface. hematite is neo-formed via soluble (Fe^{2+}) or insoluble intermediates (ferrihydrite). Generally, hematite prevails over goethite in weathering under warmer and drier climate (Allen and Hajek, 1989; Cornell and Schwertmann, 1996). Hematite is also preferentially formed in outer surfaces of rocks and on top of sedimentary profiles that are subjected to daily or seasonally changing humidity and temperature. Hematite is also commonly present as a pigment in sediments having been subjected to weak diagenesis (e.g., red beds) and in some metamorphic rocks. Such hematite is better crystalline and due to its stability, it maintains further parent rock alteration and can colour the weathering products as a relic mineral. Finally, relatively pure massive hematite of iron-ore grade can be found in nature: massive hematite has mainly been formed by oxidative pre-
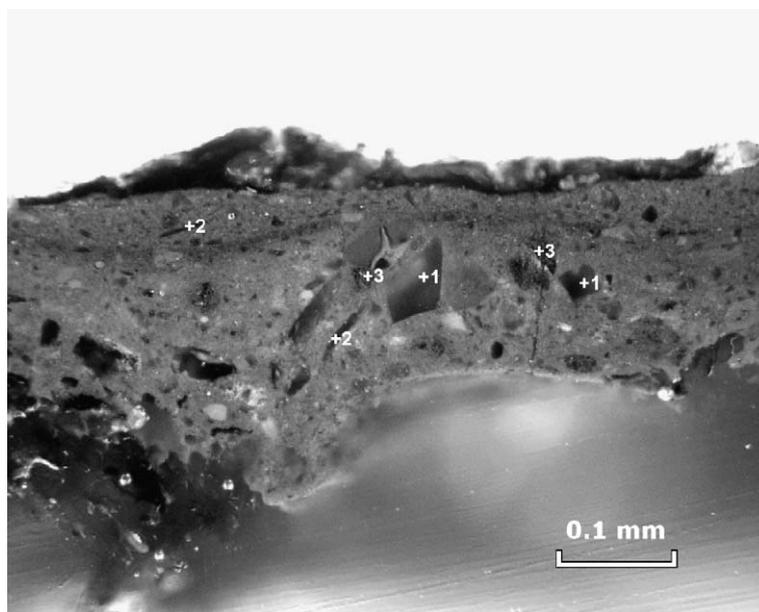

Fig. 3. Typical baroque red-orange bole ground in the cross-sectional view in the reflected light (colour information discarded); M.V. Halbax: 'Kimon and Pera' (National Gallery in Prague). Heterogenous material contains grains of relic minerals, such as quartz (+1) and micas (+2) in clayey matrix. Coarse-grained hematite (+3) could eventually indicate an additional admixture of high-grade iron-based pigment. (Obtained by OLYMPUS BX-60 light microscope, side illumination of the fragment cross-section fixed and polished in the polyester resin, photo: Janka Hradilová.).

cipitation of Fe^{2+} solutions of sufficiently stable inflow and clay minerals are hence absent.

In contrast to goethite, pure hematite has been produced artificially—at least from Middle Ages by calcination of ferrous sulphate: the crystallinity of such hematite could possibly be comparable to modern industrial reds. Coarse particles of hematite, either artificial or natural, can be sometimes revealed by optical or electron microscopy in the red-orange ground layers (boles) of baroque canvas paintings. Even if coarse-grained hematite is present beside clay minerals, it is not necessarily related to the clayey component; on the contrary, it could indicate an intentional pigment addition to the earthy material.

Bole is a word which occasionally appeared as a synonym for red ochre, but it is generally associated with Armenian bole. It is characterised as a fine red earth colour of velvety smoothness, composed of clay and iron oxide, and is used in water gilding as a ground or a gold size (Mayer, 1991). Water gilding is one of two well-known methods (along with the simpler and younger oil gilding method) that can induce a bright metallic sheen of the surface. If pink *gesso* (= gypsum pigmented by bole) or bole grounds are used, the resulting colour becomes warmer. Gilding was first used by ancient Egyptians and Chinese, and was developed to a high degree of craftsmanship during the Middle Ages in Europe, when it was used in manuscript illumination (Thompson and Hamilton, 1933; Brunello, 1975; Bartl and Lautenschlager, 2000) and in panel painting (e.g., Thompson, 1936; Plahter, 1992). The popularity of boles increased rapidly during the Renaissance and dominated in the Baroque period, when boles fully displaced white chalk and gesso (gypsum) grounds on European canvas paintings; and not in the polychrome art (Santos et al., 1998). In contrast to authors expecting the presence of greasy montmorillonite in boles (Kužvart, 1984), we usually find boles fairly kaolinitic, containing quartz, well-ordered kaolinite, mica and iron oxides, both goethite and hematite—their ratio influences the result colour, which is usually orange-red, but which occasionally can be lighter. The final hue can also be affected by extra admixtures of chalk, lead-based pigments (white lead, minium) or coarse-grained hematite. A very significant feature is a negative correlation of the potassium and titanium content as a result of different intensities of weath-
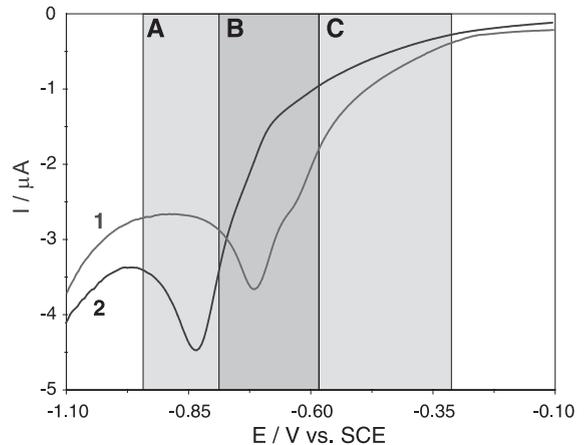

Fig. 4. Voltammetric curves of two bole grounds of *oil on canvas* paintings from the 18th century—(1) M.V. Halbax: 'Kimon and Pera' (National Gallery in Prague) and (2) Ch.A. Coypel: 'Armida is watching the destruction of her palace' (Gallery of Fine Arts in Ostrava). Regions of Fe oxides peak potentials indicate: (A) Coarse crystalline hematites (particle size >100 nm). (B) Common natural ochres (particle size ∼ 30–100 nm). (C) Umbers, some siennas (poorly crystalline, ∼ 10-nm particles). (Obtained by PC-controlled potentiostat, working conditions: acetate buffer, 3 mV/s, linear sweep voltammetry.).

ering of boles of the so-called Ti-type and K-type, respectively (Grygar et al., in press); titanium is usually present in the form of anatase. The heterogeneous appearance of the material with coarse grains of relic minerals (micas) and hematite in clayey matrix as well as the mostly angular shape of quartz possibly indicating grinding is very common (Fig. 3). A higher quality of pigment can be documented by the kinetics of electrochemical dissolution of iron oxides that reflects their crystallinity and particle size (Fig. 4). Main ingredients of the boles can also been found in their recent analogues, but the content of titanium is always lower.

5. Analytical tools and further perspectives

5.1. Clay minerals

In the practice of restoring art works, laboratory investigations help to identify the materials used in the original painting and describe the layer stratigraphy on cross-sections—that is, the factor critical for under-

standing the extent and quality of later re-paints and choosing the suitable restoration procedure. Material investigation of these rare 1- to 2-mm and extremely heterogeneous historical fragments needs selective and non-destructive techniques to be described in details. Visible light- and electron-microscopic methods seem to be most suitable for the standard analyses of the painting layers in the cross-sections revealing their morphology, texture, colour, fluorescence in UV light, and chemical composition allowing the basic identification of inorganic components (Hradil et al., 2001). Additional sampling is needed when other physical–chemical analytical methods are being used to study clay-rich pigments in detail to determine their genesis and provenance. Because of limited accessibility of historical samples, any comprehensive research on clay minerals in artistic pigments has not been done to date.

Basic identification of clay minerals by means of powder X-ray diffraction (XRD) has been minutely described, e.g. by Moore and Raynolds (1997). Difficulties with the examination of very small volumes can be solved using X-ray micro-diffraction tool, XRD working in the transmission mode (that additionally enhances the description of non-basal reflections) and using the position-sensitive detector (that also involves work with only few microgram samples). As an important additional method, electron microscopy has recently been used in mineralogical, morphological and crystallochemical investigations of clay assemblages. Transmission electron microscopy (TEM/HRTEM) operates in high resolution and makes external shapes and also internal structure of clay particles visible (e.g., Ma and Eggleton, 1999). Particle size distribution is therefore based on the conventional image analysis. Local chemical composition can be obtained via electron microprobe (AEM) and, similarly, the phase composition via selected area diffraction mode (SAED). Fourier-transform infrared spectroscopy (FT-IR) has been recently used as the method that sensitively reflects the crystallochemical composition of clay structures and its changes (e.g., Madejová et al., 1998, Madejová and Komadel, 2001). Some of these analytical procedures were also recently applied to pigment analysis in minute historical fragments (San Andrés et al., 1997; Bikiaris et al., 2000), but not in exclusively searching the clay mineralogy.

5.2. Iron oxides

X-ray powder diffraction is a traditional tool to detect and/or determine mineral pigments including Fe oxides. Aside from the mere presence of goethite or hematite, certain information on the crystallinity of these phases can be obtained and related to the pigment genesis or provenance. The detailed examination of XRD pattern of hematite and goethite reveals their particle size, possible imperfection of hematite structure due to its formation by goethite dehydroxylation (Perinet and Onoratini, 1987; Helwig, 1997), or possible poor crystallinity of goethite due to inhibitors of their crystal growth. The use of Gandolfi camera to obtain diffraction patterns of microsamples (Helwig, 1997) further enhances the applicability of XRD analysis. Although crystallinity is a generally accepted indicator of the origin of many minerals, its systematic application to Fe oxide pigments is still rather underestimated. Rock-magnetic methods, although they belong among well-established tools for detailed analysis of ferromagnetic Fe oxides (Dekkers, 1997), have unfortunately very low sensitivity to antiferromagnetic goethite. Neither is Mössbauer spectroscopy ideally suited to a detailed analysis of natural Fe oxides of a priori unknown characteristics, because non-stoichiometry, low particle size, and Al-for-Fe substitution simultaneously affect the hyperfine parameters of goethite in a complex manner (Vandenberghe et al., 2000). Mössbauer spectroscopy has been relatively frequently used to study glazes and ancient ceramics, and less commonly, pigments in cave painting (da Costa et al., 1991). Recently, this method has been used in the characterisation of iron-based pigments from historical wall paintings (Casellato et al., 2000). The applicability of Mössbauer spectroscopy could be significantly enhanced by using portable the backscattering instrument developed by Klingelhofer et al. (1998).

Spectro-microscopy is another less traditional analytical technique used recently for pigment analysis. That technique has been reviewed by Clark (1995) and later by Cooke (2000), and examples of the detection of iron-based pigments, both pure and as natural ochres in works of arts by Raman microscopy, were given by Clark and Curri (1998), Bikiaris et al. (2000) and Edwards et al. (2002). Another technique suitable to yield more information on particle size and

crystal perfectness of goethite and hematite would hence be welcome.

5.3. Voltammetry of microparticles

Fe oxides can be characterised by the kinetics of their dissolution in solutions of acids or ligands, because metal oxides reactivity is sensitive to both phase composition and crystallinity (particle size and stoichiometry). This fact is commonly used in oxalate or dithionite–citrate–bicarbonate extractions popular in geochemistry and particularly in soil chemistry (Cornell and Schwertmann, 1996). The traditional extraction methods are not suitable for microanalysis but rather for large samples. This drawback is obviously overcome in the electrochemical version of the dissolution reactivity measurements: few tenths to few milligrams of a sample is deposited on a suitable working electrode, placed in an aqueous solution and subjected to reductive dissolution by imposing reductive potential using potentiostat. The electroanalysis of powders has recently been reviewed by Grygar et al. (2002a,b). Examples of electrochemical analysis of pure inorganic pigments were first given by Lange et al. (1993). Doménech-Carbó et al. (2001a,2002) combined electrochemical and traditional techniques to pigment analysis in works of arts, showing that electrochemical means combine elemental and phase specificity, whereas EDX microanalysis is only able to detect elemental composition. In a report devoted uniquely to Fe oxide pigments in pictorial art samples, Doménech-Carbó et al. (2001b) ushered the question of more detailed analysis of crystallinity of these pigments. The principle of kinetic analysis is the visualisation of the number and type of species of different reactivity; let the species be different phases, or fractions of particles of a different size. What is important for the analysis of the mineral reactivity is the fact that both dissolution reactivity and the pigment formation by precipitation/ageing are two aspects of the same phenomenon. Morse and Wang (1996) showed that, due to Oswald ripening, metastable intermediates buffering over-saturation, and further general phenomena, authigenic minerals have usually a relatively narrow size distribution. This should also be valid for the colouring components of certain earthy pigments (e.g., ochres formed by intense lateritic weathering); but quite arbitrary heterogeneity could be expected in clastic materials (unconsolidated sediments) or even in artificial mixtures (red earths with admixtures of synthetic or grounded massive hematite). Dissolution kinetic techniques are suitable to characterise differences between specimens with the particle-size distribution function with one or two maxima, as it was shown in the case of synthetic hematite samples (Mouhandess et al., 1984).

6. Conclusions

Clayey materials, particularly extenders, priming coats and many earthy pigments are important components of the ground and colour layers of historical paintings. Their characterisation, however, is underestimated in the examination of the colour layer. The present systematic knowledge on mineral deposits and weathering crusts and the state of art of mineralogy of clays and other microparticulate minerals offer a new challenge to focus on the detailed evaluation of the clayey pigments in materials research of art works. For that, a necessary prerequisite is the recent hardware development in analytical techniques like XRD microanalysis and light, electron, IR and Raman microscopies, and several specific techniques like voltammetry of solids.

Typical questions regarding clays and earthy pigments in paintings are as follows:

- Presence and crystallinity of kaolinite and Fe oxides as typical markers of the intense weathering;
- Presence and kind of expandable clay minerals, which could eventually cause the damage of painting layers because of clay–water interactions and volume changes;
- Mineralogical composition of green earths (glauconite, celadonite, or other minerals);
- Identification of non-clay components in earthy pigments, such as gypsum in the '*gesso*'-type ochres and other mostly artificial admixtures indicating a path of preparation.

In the case of Fe oxides, the detailed examination of their crystallinity combined with the mineralogy of their matrix can allow analysts to distinguish their

natural or artificial origin. The general aims of that effort are (i) to contribute to the knowledge of the materials provenance, (ii) to learn more about the historical pigment markets and painting techniques, and finally (iii) to examine the diagnostic power of the earthy pigments in comparison to the well-established 'marker' pigments related to certain historical periods.

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