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CLAY MINERALS IN PIGMENTS OF MEDIAEVAL AND BAROQUE PAINTINGS

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Abstract: Six different pieces of gothic wooden panels or sculptures and baroque canvas paintings were chosen to identify the content, mineralogy and crystallinity of clay minerals present in pigments of original grounds and painting layers. Electron microscopy and microanalysis, X-ray diffraction and electron diffraction have been used to investigate minute heterogeneous material fragments. Reference commercial clay-rich pigments have also been measured. The greyish basal layer of some chalk grounds of gothic paintings and sculptures is more siliceous than expected with only a low content of clays. Baroque bole grounds are rich in clays, they contain predominantly kaolinite, mostly well-ordered; illite is common, smectite was enriched especially in the ground of a Baroque painting by Ch. A. Coypel.

Key words: Gothic and Baroque paintings, bole grounds, ochres, clays, earthy pigments, chalk.

Introduction

Within the art restoration process, material fragments are investigated in the laboratory with the aim to identify pigments and binding media used in the original painting and to describe the stratigraphy of re-paints on cross-sections, which is important for choosing suitable restoration procedures. Materials research on heterogeneous fragments needs instrumental techniques to be used for their detailed description. We have found optical and electron microscopic methods to be the most suitable for the standard identification of inorganic components in the painting layers regarding their morphology, texture, colour, fluorescence in UV light and chemical composition as it is documented on the multiple of research reports of the last years (e.g. Hradilová & Hradil 2001). Additionally, powder X-ray diffraction analysis (XRD) is used if well-separated homogenous samples are available in a sufficient amount. In the present study, we have focused on the detailed classification of earthy pigments (white, yellow, red, brown and green), known in the painting technology as ferric ochres, siena, umbra, terra verde etc. These pigments are found either in painting layers or in clay-rich grounds. Red clay grounds, known as boles, represent one of the most typical features of Baroque painting technique.

Scientific works referring explicitly and systematically to the ground materials (and therefore also to clays) of mediaeval and Baroque paintings have not been found in the literature. General information and classification criteria are given only in the universal monographs concerning painting techniques, for example, in Laurie (1967), Harley (1982) or, in the Czech literature, Slánský (1953 and 1956). Natural clay minerals as pigments and ochres are shortly dealt with in the monograph of Konta (1995). The authors obviously derive from historical sources, today accessible in reprints, for example from Cennini (1946), Berger (1988) or Eastlake (1960). Grounds, as coating materials used to prepare a surface of panel or canvas for painting, can be subdivided according to binding media such as glue, emulsion, oil grounds or, evidently, according to the inorganic components as chalk, gesso or bole grounds. If we neglect frescoes as paintings traditionally built on ‘plaster grounds’, historically, 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 (Bentchev & Haustein-Bertch 1997). In medieval Europe, grounds applied on wood panel surfaces were already very common.

Iron-rich pigments replace white chalk and gesso in the grounds of painting of the 16th century and, generally, they are predominant in Baroque works of the 17th and 18th centuries in all European countries (Santos et al. 1998). In a narrow sense, the term ‘bole’ is related to the hygroscopic smectite-rich material coloured by iron oxides (‘Armenian bole’) and used especially as a ground for the gilding (Kužvart 1984). Generally, this term is used for any iron-rich ground, typically red or orange-red, probably rich in hematite, but commonly in casts ranging from yellow (goethite-rich yellow ochre pigments) to brownish, if containing some manganese oxides (siena and umbra pigments). Earthy pigments occur in nature (i) as residual laterites after intense weathering of rock-forming silicates with silica removal or just after oxidation of iron sulphides as mineral ochres in oxidation zones, overburdens and tunnels in mining areas, or, (ii) dislocated from the source area in sedimentary deposits of coloured clays. To distinguish among these materials, used in a relatively long historical period and large territory, it is necessary to describe clay minerals and iron oxides in detail; their mineralogy reflects weathering conditions and should be different case to case.

Within this study, powder X-ray diffraction (XRD), scanning electron microscopy/microanalysis (SEM/EDX) and partially also transmission electron microscopy are used to identify and compare clay minerals in real historical painting fragments and in reference pigment and clay standards of natural origin.

Materials and methods

Reference commercial pigments from different providers are stored in collections of the School of Restoration of the Academy of Fine Arts in Prague. Powders of earth pigments from this source are mostly declared as natural analogues of historical materials. As we have found earlier (Hradil et al. 1998), some of them do not meet this definition because of artificial admixtures, for example, of barite involving additional tonality of the pigment. X-ray powder diffraction has been employed for mineralogical analyses of these samples using a SIEMENS D-5005 instrument under the following measurement conditions: CuKα radiation, secondary monochromator, voltage 40 kV, current 30 mA, degree range 2θ 3–90°, step 0.02° per 8 seconds. The raw data were processed by the ZDS for Windows program (Ondruš 1997) employing diffraction pattern database (JCPDS 2000). Clay minerals were described using conventional rules described, for example, in Moore & Reynolds (1997).

Fragments of historical paintings have been collected and treated in the following way: after wary sampling realized by qualified restorers, fragments were pre-treated by casting them into moulds of a polyester resin. Polished cross-sections were then prepared on the Kompakt 1031 device to catch the complete layer stratigraphy. Beside observations in the optical microscope Olympus BX-60, the scanning electron microscope Philips XL30 CP was used in arrangement with Robinson detector of back-scattered electrons and EDAX detector of X-rays. If possible, a small part (up to 10 miligrams) of raw material was separated, homogenized and measured by powder X-ray diffraction method and, in some cases, also by transmission electron microscopy; transmission electron microscope Philips EM 201 enables obtaining of electron diffraction patterns of crystyalline solids.

Within this study, we have chosen six different pieces as examples — gothic wooden panels and sculptures by Master Theodoricus (National Gallery in Prague) and unknown painters (Courtauld Museum of London), Baroque canvas paintings by J. Hess (Church of Our Lady Victorious in Prague), Ch. A. Coypel (Gallery of Fine Arts in Ostrava), M.V. Halbax (National Gallery in Prague) and an unknown painter (Castle Sychrov).

Results and disscusion

Reference pigments

On the basis of mineralogical composition, reference earth ochres of today's commercial production can easily be sorted into groups referring to their origin as (i) French ochres with dominant content of kaolinite and quartz, accompanied by clay mica (illite) and hematite or goethite, (ii) German ochres also with quartz, kaolinite, illite and hematite (or goethite), but usually accompanied by calcite and/or dolomite and (iii) Italian ochres with dominant amounts of gypsum and anhydrite, usually also calcite, pigmented by goethite or hematite and accompanied by smectite group minerals and minute amounts of kaolinite. Differences in the diffraction patterns of commercial French and Italian ochres are shown in Fig. 1. Other unspecified ochres are similar in some content of clay minerals, but differ significantly in crystallinity and content of artificial additives. Samples marked as 'green earth' are usually rich in glauconite (or celadonite), hematite has been found as an admixture.

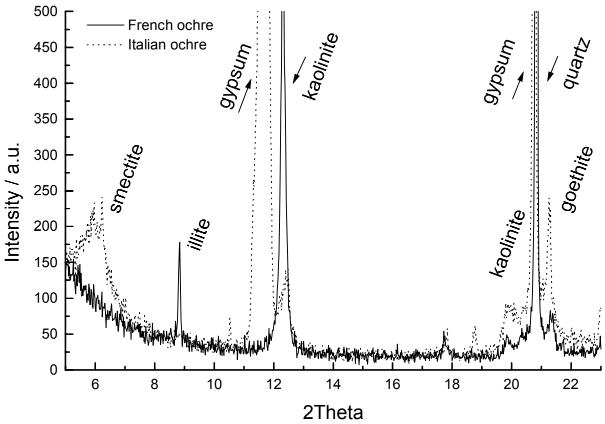

Fig. 1. Part of diffraction patterns of commercial pigments: a comparison of French and Italian ochres.

Clay minerals in paintings of the Middle Ages

The first indication of any content of clays in the studied fragments is given by the analysis of layer stratigraphy and chemical composition on polished cross-sections by means of scanning electron microscopy equipped with a Robinson detector of back-scattered electrons and EDAX detector of X-rays. The relative contents of aluminium and/or magnesium with respect to silicon involve evaluating the appropriate portion of aluminosilicates within the mixture. In the mostly chalk grounds of a number of Gothic wooden panels and sculptures a greyish basal layer has been identified. This grey chalk, usually termed "mountain chalk" is classically interpreted in painting technology as a clay-rich chalk (silt) pigmented by natural bitumens or graphite.

As we have found in the ground of a Gothic painting by Master Theodoricus 'St. Bishop' (National Gallery in Prague), as well as in the ground of a Gothic wooden panel 'The Crucifixion' (unknown painter, Courtauld Museum in London), the relative content of aluminium within this basal layer is relatively small and the layer composition should be interpreted as more siliceous. Independent measurement provided by powder X-ray diffraction on fragments of similar ground layer breakaway from the cracked surface of a Gothic polychromed wooden sculpture 'Madonna from Pilsen', has identified only calcite and quartz as the main components. We have concluded that the composition of the basal greyish layer typical in some gothic chalk grounds especially those of Czech provenance does not meet the definition of 'mountain chalk' and the content of clays is lower than expected.

Clay minerals in baroque paintings

Most of measured Baroque bole grounds are aluminium-rich, as in the case of the ground of altar piece by Jan Hess: 'St. Theresia' (Church of our Lady Victorious in Prague), which contains mainly Si, Al, Fe, K, Ti and Ca. It represents a typical composition of red ochres used in grounds of Baroque paintings; besides aluminium and silicon, usually potassium and sometimes magnesium occurs as building elements of clays, iron occurs mostly in oxides. Titanium oxides of natural origin are also very common and could refer to similar associations and sources of these materials — they have not been found in any of the reference commercial pigments.

Mineralogical composition is difficult to distinguish if operating with only minute material fragments. However, we have obtained interpretable diffractions, if the fragment was pretreated in a drop of toluene applied on the silicon slide, dried in air and measured. Thus we have distinguished between smectite-rich and kaolinite-rich grounds, as it is clearly visible from the comparison of diffraction patterns of samples from the paintings by Ch. A. Coypel ('Armida watching the destruction of a palace') and by an unknown painter ('Portrait of the sitting lady'), (Fig. 2). Identification of smectites in grounds is important because traditional historical source material — Armenian bole — should be a montmorillonitic clay with hygroscopic properties (e.g. Kužvart 1984). In our findings, kaolinite is usually dominant. For example, the bole ground of the painting 'Kimon and Pera' by M.V. Halbax contains predominantly well-ordered kaolinite accompanied by quartz; titanium oxide can be undoubtedly identified as anatase (Fig. 3).

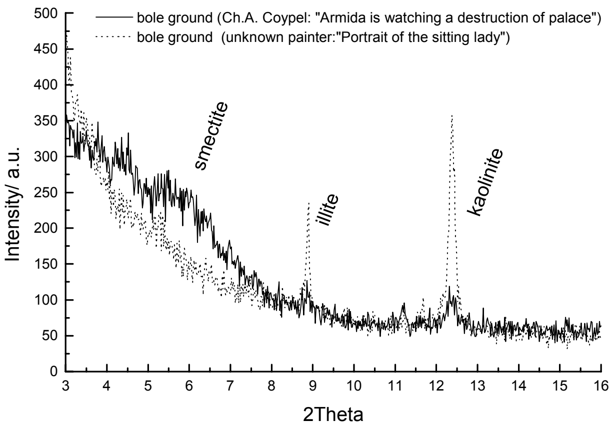

Fig. 2. Part of diffraction patterns of historical bole grounds: a comparison of two Baroque paintings (by Ch. A. Coypel and unknown author, respectively).

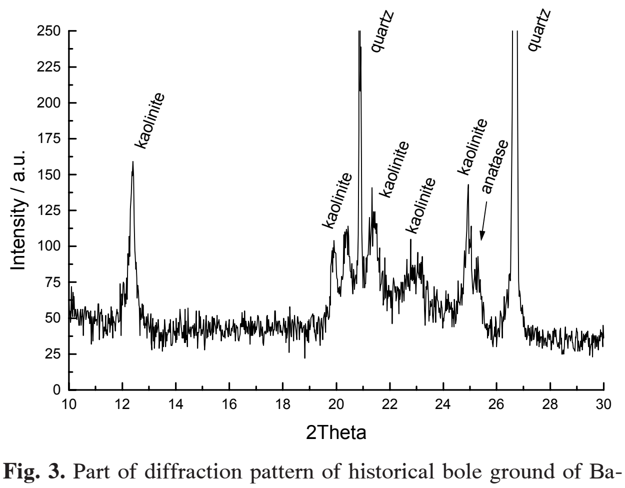

Fig. 3. Part of diffraction pattern of historical bole ground of Baroque painting of M.V. Halbax with well-ordered kaolinite.

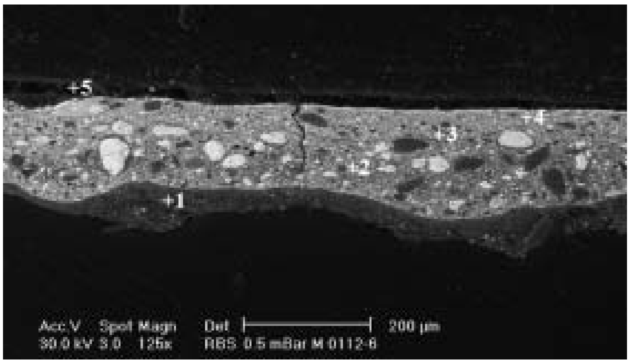

Fig. 4. SEM image (back-scattered electrons) showing a cross-section of painting layers of the painting *'Armida watching the destruction of a palace'* by CH.A. Coypel. Layers have been interpreted as: **(1)** Bole ground (smectite, kaolinite, illite, anatase, quartz, well-crystallized hematite), **(2)** Underpainting (brown siena containing clays and Mn and Fe oxides, white lead, bone black), **(3)** White lead, grains of green earth (celadonite — because of higher Mg/Al ratio), **(4)** Dtto 3 + grains of Naples yellow, **(5)** Lake double-layer (dammar with copal in poppy oil).

As a case study, the complete interpretation of original painting layers of the Baroque painting by Ch. A. Coypel 'Armida watching the destruction of a palace' is shown in Fig. 4. Beside the bole ground, clays also occur in painting layers as a main substance of Mn-rich grains of siena and as a mineral celadonite (green earth grains). A full description has been done on a cross-section of the painting 1 mm thick, which contains five different layers (Hradilová & Hradil 2001).

Conlusions

When studying the chemical composition, mineralogy and crystallinity of clay minerals within minute fragments of original historical paintings from the Middle Ages and Baroque, we have found that:

— greyish basal layer of some chalk grounds of Gothic paintings and polychromed sculptures known as 'mountain chalk' is more siliceous (quartz-rich) than expected; the content of clay minerals is low;

— Baroque bole grounds contain predominantly kaolinite (as measured on four different pieces), interpreted mostly as well-ordered; illite is frequent, smectite was enriched in the ground of a painting by Ch. A. Coypel from the Gallery of Fine Arts in Ostrava; grains of the green earth found in the same painting contain celadonite.

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