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Research paper

Kaolinite-alunite association in late Gothic white grounds from Slovakia: A local peculiarity in painting technology

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ABSTRACT

In European Gothic paintings, the use of materials other than calcium carbonates (chalk) or calcium sulphates (gypsum) in painting preparations was rare. Therefore, alternatively used materials, such as, e.g., white clays, can be seen as peculiarities, which correspond to the local availability or artist's preference. In this study white chalk-based grounds from masterpieces attributed to the workshop of Master Paul from Levoča, Slovakia, were investigated. It was motivated by the assumption of restorers that Master Paul complemented the chalk ground by more malleable white clay to achieve a very fine modelling of his polychrome statues. The results were compared with other artworks, where the use of white clays in grounds was previously indicated, and with reference samples of kaolin from Central-European sources. It was found that detailed microanalysis of the white earths in paintings leads to distinguishing of regional provenances. While in Czech paintings, either from Gothic or Baroque periods, residual kaolins from West-Bohemian deposits were identified, in the late Gothic Slovak paintings white earths came from hydrothermal kaolin deposits situated, most probably, in Tokaj Mountains, Hungary. Here presented finding is probably the first ever evidence of natural alunite and hydrothermal kaolinite in painted artworks, where they were applied as white pigments.

1. Introduction

1.1. Painting grounds

As previously reported (Hradil et al., 2015), the internal structure and sequence of individual preparatory and painting layers of historical paintings and wooden polychrome statues were defined by very strict rules. On the support of choice (wood or canvas), a ground layer is usually applied to flatten its surface. A thin insulation layer separates this ground from subsequent colour layers that eventually include a preparatory drawing and/or priming (imprimitura) followed by consequent layers of paint. In the traditional European art several types of grounds appear on panel and easel paintings – white gypsum-based or chalk-based (from Byzantium to Gothic period), and colour clay-based (typically in Baroque) (Hradil et al., 2015; Stols-Witlox, 2012).

Among white soft rock materials, which were suitable for making grounds, the chalk was prevailing in regions “north from the Alps” and gypsum in regions “south from the Alps” - particularly in Italy and Spain (Stols-Witlox, 2012). For the eastern regions, this division was not so sharp. For example, the white gypsum grounds were found in late Gothic altars in Transylvania, which may be related to the use of local source of the material (Serendan et al., 2013). In the Gothic period, the use of other materials in painting preparations, such as, e.g., white clays, was rare. For example, the use of kaolin in the preparatory layer was already described in Gothic wall-paintings, but never in the panel painting. In west Bohemian Gothic murals, the kaolin was used as an alternative material to the most frequent limewash as a result of easy local availability of the material and its better technological properties (Švarcová et al., 2011).

1.2. White earths

Kaolin, known as “China clay”, is widely reported in antiquity, particularly in China and Japan, where it was used rather extensively in the priming for clay wall paintings (Gettens and Stout, 1966). Pure kaolin was also used as a white pigment in the rock art, e.g. in South Africa or Australia (Eastaugh et al., 2004). Although the mineral kaolinite - $Al_2Si_2O_5(OH)_4$ is a common component of coloured earth pigments, such as, e.g., red or yellow earths, its use for a pure white colour occurs only rarely in the historical European painting. Kaolinite-

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rich earths, known as “boles” were used as preparatory layers – poliments for water gilding (Barata et al., 2015; Hradil et al., 2016), but their colour was most frequently red or red-orange. White boles, which were represented by pure kaolins, have been only rarely described, particularly in Italian Renaissance art (Powell and Allen, 2010). Red bole imparts a warm tone to gold leaves, which is most attractive. White bole turns the final tonality of the gilding to slightly greenish.

Coremans and Thissen (1964) has identified “kaolin” in the ground of the canvas painting known as “*Stuttgart Self-portrait*” by Rembrandt (1606–1669), but its technological function is not very clear. Rembrandt himself, like many other authors in the 17th century, experimented with chromaticity of grounds and applied them in several differently coloured layers. The majority of Rembrandt's canvases are primed with a double ground. The first layer is represented by a red-orange ochre bound in oil and the second grey layer is made from lead white ($2PbCO_3{\cdot}Pb(OH)_2$) mixed with chalk, ground in linseed oil, and one or more other pigments (Elliott, 2007). It is highly probable therefore, that kaolin was a part of natural earthy material, while a brighter colour was specifically achieved by adding lead white to the chalk. Flanders at that time was famous for its cheap lead white production, so its addition to grounds for getting white seems logical.

Different example can be given in painting grounds by most significant Czech early Baroque painter Karel Škréta (1610–1674), who tried to apply similarly composed double layered construction with red-orange layer at the bottom and a white-grey layer above. Škréta however, unlike the Rembrandt, applied kaolin instead of lead white, because in that time residual kaolins were easily accessible in West Bohemian regions (Hradil et al., 2010). These cases show that the white clays – kaolins represent rare materials in historical European painting and their finding has always a significance in the art-historic context - whether their use is related to the local availability of raw materials, or to their technological characteristics and/or preferences of the artist.

In general, white clays (or white earths) in the fine art are widely represented by residual kaolins, because of their easy availability in higher amounts and sufficient uniformity in colour, granularity, homogeneity and purity. On the other hand, the use of hydrothermal kaolins, and also other clays, such as, e.g. white bentonites, was probably limited, but there is still lack of evidence for it.

In this study white chalk-based grounds from masterpieces attributed to the workshop of Master Paul from Levoča (Leutschau), Slovakia, were investigated. It was motivated by the assumption of restorers that Master Paul complemented the chalk ground by more malleable white clay to achieve a very fine modelling of his polychrome statues. The primary objective of the research was to verify this assumption.

Fig. 1. Polychrome statue of St. John the Baptist from the St Johns' altar at the St. James church in Levoča, Slovakia (J1607), dated to around 1520, attributed to Master Paul from Levoča.

2. Materials and methods

2.1. Samples

Micro-samples containing white grounds were collected from a total of 4 works of art attributed to Master Paul from Levoča and his workshop. It included 4 samples from polychrome statues on the main Altar at the St. James Church in Levoča, Slovakia (J1608), which is the world's highest (18.62 m!) Late Gothic altar created in 1508–1517, then 9 samples from the side St. Johns' Altar at the same church (dated to 1520) – both from the polychrome statues (J1607) (Fig. 1) and altarpieces (J1606), and finally 6 samples from the polychromy on wood “*Crucified Christ*” at Spišské Vlachy, Slovakia (J1605), dated again to 1520. Other white grounds, which probably also contain white clay, were investigated within comparative studies. It included 2 samples from the painting by Karel Škréta (1610–1674) named “*St. Charles Borromeo attend the plague-stricken in Milan*”, National Gallery in Prague, Czech Republic (J1020) and 7 samples from the Gothic murals in Bor near Karlovy Vary, Czech Republic (J0915). In our previous study, the white clay from the Gothic murals has already been classified as residual kaolin from a local source at Karlovy Vary area; this classification was based on similarity of their crystallinity indices (Švarcová et al., 2011). Details regarding the painting technique of the studied artworks can be found in the unpublished reports by Hradilová J. et al., 2016, which are archived in ALMA laboratory at the Academy of Fine Arts in Prague. List of all analysed microsamples with their brief description is given in Table 1. As a reference material, rock samples from the Király Hill quartzite quarry at Mád, Tokaj Mts., Hungary, have been collected (Fig. 2). It represents a hydrothermal kaolinite deposit in altered rhyolite tuffs (Bajnóczi et al., 2002). As a reference, chemical composition of kaolins from Otovice deposit in Karlovy Vary area, Czech Republic, has been adopted from Aron (2000).

2.2. Light and electron microscopy

Olympus BX 60 light microscope equipped with Olympus DP 70 digital camera and/or Zeiss Axio Imager A.2 light microscope with the Olympus DP 73 digital camera were employed for visual observation of