Review

Clay Minerals in European Painting of the Mediaeval and Baroque Periods

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Abstract: Clay-based pigments are among the most traditional. Unlike other mineral pigments, they have never been fully replaced by synthetic analogues and are still used in painting today. Since their analysis requires a specific approach, detailed distinction of clay pigments has never been a part of routine chemical-technological research in fine arts—regardless of a great potential of clay minerals for determining regional provenance of the material. This review article maps and summarizes research on clay pigments in historical paintings that has been systematically pursued by authors since the beginning of this millennium. This rallying and interconnection of knowledge was an opportunity for a new reflection on the common aspects of these research projects, either methodological or interdisciplinary, since these findings are closely related to art-historical evaluation of artworks. It offers a comprehensive insight into the microanalysis of clay pigments with using powder X-ray micro-diffraction and complementary methods. Significant new findings come, for example, from research on the Italian Baroque. It becomes clear that cheap availability of raw material, pottery clays, could have played an important role in the change in painting technology at the turn of the 16th and 17th centuries.

Keywords: earth pigments; ochres; clay-based grounds; powder X-ray microdiffraction; provenance studies; pottery clay; kaolin; painting; gilding

1. Earths and Ochres—A Brief Overview

Clay and iron oxide pigments are among the longest-used mineral pigments. They occur in prehistoric art and are still used up to the present days. In particular, this is due to their cheap availability in nature, but also to their outstanding properties, such as colour stability and high adhesive power [1]. Recently, a very comprehensive and up-to-date overview of rock art pigments has been published [2]. The first painters worked with four main colours to create their pictures in caves: yellow, red, black, and, later, white. Kaolin, chalk-calcite and gypsum (Appendix A) were applied for white, hematite (Appendix A) for red, various ochres for yellow and carbon-based materials, calcined bones or, eventually, manganese/iron oxides [3] for dark shades. Green and blue shades appeared later, and although iron was the predominant colouring agent, minerals containing Cr have also been documented [4]. While green Fe-rich clay minerals (celadonite or glauconite, Appendix A) were available in various places in nature, obtaining an intense blue colour was only rarely achievable with clays. The only blue silicate mineral (but not clay)—aerinite (Appendix A) was evidenced just in Romanesque wall paintings in Pyrenean region [5] and, according to the latest research, also in north-west Italy [6]. In pre-Columbian America, ancient Mayans mixed extracted plant dye indigo

with muddy water, and after drying they obtained a highly stable turquoise-blue pigment known as Maya blue (Appendix B). Although no historical sources describing the preparation of the pigment in a more exact way are available, the purpose and technology of making are widely discussed in the literature [7]. Only in modern times it was found that the enormous stability and peculiar hue of the pigment result from the intercalation of indigo molecules into the channel structure of the clay mineral palygorskite (Appendix A), which predominated in the mud. The location of the dye molecules on the clay support, as well as the origin and variability of the colour, are still not fully understood, although they have been studied extensively since the 1960s [8–11]. In any case, this is one of the very first examples of targeted intercalation of clays by organic molecules in order to get hybrid materials-organoclays with new useful properties [12], such as stable colour which persists even at high temperatures and in an aggressive chemical environment [13]. This shows that clays can serve not only as pigments but also as pigment carriers or as various types of fillers in paints. In the fine arts, for example, kaolin was also rarely used as a substrate for the precipitation of plant dyes [14] (beside more frequent potassium alum).

Clay and iron oxide pigments represent a very wide range of materials and, therefore, use of correct terminology is very important. Ochre, earth, and clay pigments are often used as synonyms covering the same group of materials, but this does not correspond to reality. Not each ochre is clay and not each earth has an ochreous colour. One has to consider that in addition to ochreous clay materials, there is also a number of ochres containing only Fe (oxo)hydroxides and (almost) no clay minerals. Further, since the term "ochre" is originally derived from the colour, using the term "red ochre" (very frequent in the literature [15,16]) is as meaningless as "ochreous red". The terms as "red earth", red iron oxide" or "iron red" have rather to be used instead.

From the mineralogical point of view, "white earths" are represented mostly by kaolins (with a predominant content of kaolinite) and "green earths" by green clay micas (celadonite and glauconite, Appendix A). "Red, yellow and brown earths" represent a large group of materials, which are coloured with free iron oxides (or also Mn oxides), in particular by goethite and/or hematite [1]. Experts engaged in the research of historical paintings tend to classify pigments by the colouring agents, as, e.g., Pb-based, Cu-based, Fe-based, but it may not be sufficient for polymineral natural mixtures. Since the colouring agent in red, yellow and brown earths is, in most cases, goethite or hematite (much less frequently also jarosite or other phases, Appendix A), the clay minerals remain rather overlooked—although they can form the predominant part of the material. However, the diversity of clay minerals can be decisive for assessing the origin of the pigment, or even its regional source.

2. Methodology of Clay Pigments' Microanalysis

The analysis of pigments in paintings is motivated not only by studying the palettes of individual painters, but also by an effort to refine the dating or to determine the provenance of anonymous artworks. Earth pigments, however, have always been considered to be poorly suited for the provenance studies, precisely because of their occurrence "always and everywhere". The other reason was the lack of an appropriate methodology. Provenance studies of ochres and earths are more frequent in the investigation of prehistoric art, which is mainly due to the greater availability of material for analysis. These studies are most often based on the analysis of trace elements; the descriptions of clay structures are not solved [17]. In later periods (especially from the Middle Ages onwards), provenance studies are almost exclusively art-historical. Only very small and heterogeneous samples (typically containing also numerous overpaints, retouches and conservation treatments) can be taken from vivid and compact paintings, and since their non-destructive mineralogical analysis is difficult, a closer description of earth pigments in these cases is practically absent in the scientific literature. A non-destructive approach to the analysis of fine arts is highly preferred since the samples are rare and highly valuable.

The preparation of paint fragments (whose dimensions most commonly do not exceed 1 mm) typically includes their embedding in synthetic resin, cutting to get a cross-section, which is considered to be a "standard" specimen—the stratigraphy of paint layers can be easily described on it and

further analyses are performed on individual layers (Figure 1). Only in some cases the material obtained is large enough to be split to more fragments and some of them can be analysed separately without any pre-treatment. The analytical procedure usually involves optical microscopy followed by semi-quantitative elemental analysis (e.g., by scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS) or micro X-ray fluorescence (micro-XRF)), and by spectroscopic analyses of pigments and binders by Raman and Fourier transform infrared micro-spectroscopy (micro-Raman, micro-FTIR). None of these methods leads to the differentiation of individual clay minerals in an unknown polymineral mixture due to their variable chemical composition, structural similarities, and low Raman scattering. While micro-Raman can help in the differentiation of clay minerals in white and green earths (as, e.g., celadonite vs. glauconite [18]), it is almost unusable for the earths coloured with Fe oxides. The weak Raman signal of alumosilicates is largely suppressed in the presence of simple oxides that scatter more. As a result, hematite and/or anatase and/or quartz (Appendix A) can be recognized in the spectra, but not the predominant clay minerals [19]. Thus, the Raman spectroscopy never gives complete information about the composition of earths [20], but in specific cases it can be useful. Particularly, Raman spectroscopy coupled with SEM-EDS can be mentioned as one of today's hybrid devices, which also looks very promising for the field of mineralogical analysis of artwork microsamples in general [21,22]. Coloured earths and ochres of various origins are not differentiated, because only hematite and/or goethite were identified.
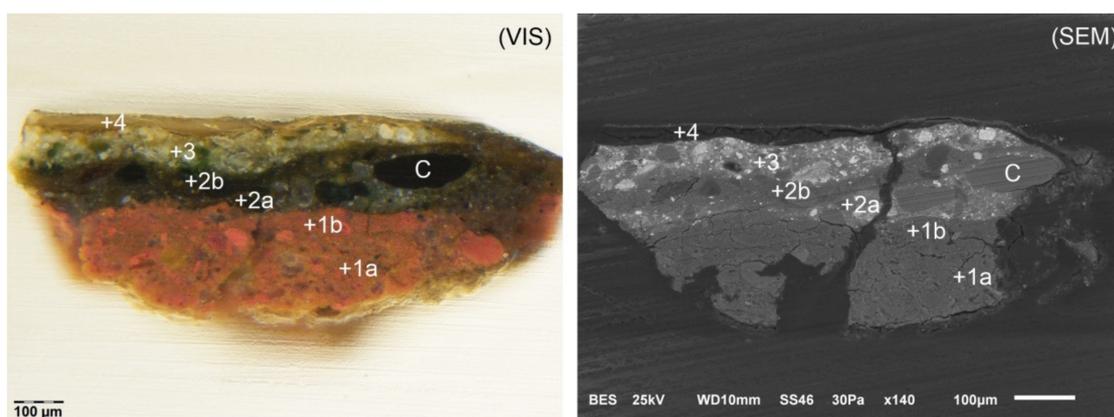
Figure 1. Micro-section of the sample from oil-on-canvas painting *Still life with fruit*, Museum of the Wallachia Region, Lešná Chateau, Czech Republic, unknown painter from the end of 17th century, in visible light (VIS) and back-scattered electrons (scanning electron microscopy; SEM), in which various clay minerals in grounds and painting layers are manifested; +1 double layered clay-based ground containing beige pottery clay (with chlorite, illite, quartz and carbonates, Appendix A) and red-orange earth (containing a specific interstratified illite/smectite, kaolinite, goethite, hematite and quartz, Appendix A); +2 green double layer containing large grains of the green earths (celadonite of Molte Baldo type, Verona, Italy, the largest grain indicated by "C") mixed with Naples yellow, massicot (Appendix B) and other unspecified earth pigments; +3 layer of lead-tin yellow, lead white, and massicot (Appendix B) coloured by green earth (again pure celadonite) and common yellow earths; +4 varnish. (Obtained by Zeiss Axio Imager A.2 light microscope (Carl Zeiss Microscopy GmbH, Jena, Germany) with the Olympus DP 74 digital camera (Olympus, Tokyo, Japan) for VIS, and by scanning electron microscope JEOL JSM6510 with detectors (Jeol, Tokyo, Japan) of back-scattered electrons for SEM, coupled with an INCA energy dispersive spectrometry (EDS) detecting unit to describe the elemental composition of individual layers and grains; photo with permission from Janka Hradilová and Silvie Švarcová; mineralogical analysis was performed on untreated fragment and cross-section by PANalytical X'Pert PRO diffractometer (Malvern Panalytical, Almelo, the Netherlands) equipped with a CoKα X-ray tube-point focus, X-ray mono-capillary with diameter of 0.1 mm and a multichannel detector X'Celerator (Malvern Panalytical, Almelo, the Netherlands) with an anti-scatter shield).

To identify individual clay structures, it is necessary to apply powder X-ray micro-diffraction (micro-pXRD), which is the only method requiring no special pre-treatment of "standard" microsamples from paintings (paint fragments and their cross-sections). Although other alternative methods look highly promising for the future (transmission electron microscopy—TEM, particularly in high resolution—HRTEM), they usually require material separation and a special procedure of preparation (which cannot be performed in all cases). Besides the common limitations of micro-pXRD (such as, e.g., worse resolution, more pronounced effect of heterogeneity in small irradiated volumes, etc.) [23], there are several other phenomena that should be considered to avoid misleading interpretation of micro-diffraction patterns. Most of the special procedures designed to distinguish individual clay minerals (as, e.g., ethylene-glycol solvation, etc., [24]) cannot be performed on micro-samples. Instead, different expandable clay structures can be recognized by characteristic shifts of their diffraction lines, which appear during the preparation of colour mixtures as a result of interaction with organic binders. The model experiments already showed that proteinaceous binders (animal glue, egg white) cause an increase of the basal spacing (which is relative to the content of smectite layers in the material) (Figure 2), while the presence of fatty compounds (in oils or egg yolk) results in its very slight decrease. In both cases, a subsequent dehydration of the structure was prevented [25]. The accuracy of quantitative microanalysis of clay minerals in mixtures with other minerals in earth pigments is characterised by total bias values in the range of 3–10 wt.%, while in the case of conventional Bragg–Brentano geometry, the total bias does not exceed 6 wt.% [25]. Although the laboratory micro-pXRD patterns usually have worse resolution and higher noise that synchrotron radiation X-ray diffraction (SR-XRD), they allow even the calculations from non-basal diffractions—for example, the calculation of crystallinity indices [26].

Correct differentiation of clay structures is just the first step in the classification of clay-based artistic materials according to their provenance. The micro-pXRD results must be further supported by at least one independent method. Characteristic ratios of the main elements (as, e.g., K/Ti or Al/Mg) [27,28], trace element contents (obtained, e.g., by laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) [29]) or micro-paleontological analysis (for calcareous clays) [30] can serve as an additional criterion. The following examples show combinations of these methodological approaches and the results obtained.
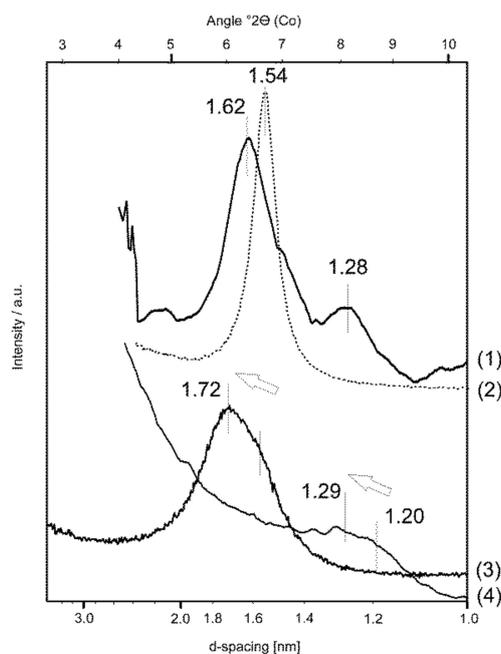
Figure 2. Part of diffraction patterns of the ground of the painting by Italian Baroque painter Antonio Zanchi (1) and the reference Ca-montmorillonite SAz-1 [31] (2) (Appendix A), which do not match very

well; a better match is obtained with two modified structures resulting from model experiments—Ca-montmorillonite SAz-1 after a short term interaction with a proteinaceous binder (3) and interstratified illite/smectite with. approx. 40% of smectite modified in the same way (4); shifts of diffraction lines after mixing the clay with the binder are indicated by arrows (according to [25], obtained by PANalytical X'Pert PRO diffractometer equipped with a CoKα X-ray tube-line focus for reference clays, or point focus + X-ray mono-capillary with diameter of 0.1 mm for the microsample; and a multichannel detector X'Celerator with an anti-scatter shield).

3. The Story of Armenian Bole

In traditional painting technology, the term "bole" simply means a high-quality red clay. The quality is not solely derived from the colour, but also from a high adhesive power, which allows the bole to serve as an adhesive support for a thin metal foil—typically gold, silver or *Zwischgold* (two-sided metal foil made by adhering a gold leaf over a silver leaf). This technique is known as water gilding on poliment (= a preparation adhesive layer) and old treatises published in the turn of the 14th/15th century (written by Johannes Archerius and Cennino Cennini [32,33]) count for this purpose with the so-called "Armenian bole". Armenian bole from its original location is considered to be a montmorillonitic red clay from a specific source in former Armenia [34]. It resembles the same material as that used for medicinal purposes since Antiquity, because the first usage of the term "bole" (or "bolus") had been reserved for clays which were strongly absorbing and had been employed as antacids and antidiarrheal agents [35]. The question is whether it has always been (for both applications and throughout the whole history of European painting) clay from the same source or at least clays of similar composition and properties. It does not seem very likely, because medicine and painting had quite different requirements for material properties. While high smectites content is beneficial for medicinal purposes (because of alkalinity and strong absorption capacity), in paints, it could cause mechanical instability (due to swelling effects under increased humidity). On the other hand, other properties of the material, e.g., elasticity, formability, or intense red colour, were sought by painters and goldsmiths, and therefore, the boles were more likely represented by various mixtures of minerals [36]. Finally, the question of material availability should also be taken into account—particularly in the case of clay materials, which are extracted in many places, and thus showing significant differences in prices with respect to the transportation distance.

According to the latest results, for example, there is a clear difference in the mineralogical composition of Mediaeval poliments used in the 14th and 15th century and those of the early Renaissance (late 15th and early 16th centuries) [36]. In various regions of Central Europe (Bohemia, Bavaria, Transylvania, Upper Hungary-Slovakia), alternative materials suddenly began to be used at that time, having a composition more corresponding likely to bauxites (with gibbsite and/or boehmite, Appendix A) than clays [37,38]. This change was probably related to the availability of a new raw material, which, however, exhibited worse technological properties. A low clay minerals content did not provide sufficient adhesion, which led to the necessity of adding more organic binder—the layer thickness increased. Neither was the red colour intense enough, which led to an additional colouring (with extra hematite or cinnabar, Appendix A) (Figure 3). Since the poliments are very thin layers, it is not possible to analyse them by micro-pXRD method from the sample cross-section. Only the gildings, which are not covered by later overpaints (or over-gildings), can thus be analysed as untreated fragments. Their top surface is measured in places, where the metal foil is damaged and abraded and the response from the poliment is higher. In all other cases, when micro-pXRD cannot be applied, clay and bauxite poliment types can be (although only tentatively) differentiated according to characteristic Si/Al ratio. In natural clays, this ratio (calculated in at.%) is always higher than 1 (with the exception of very pure kaolinite, where it is equal to 1) and becomes lower than 1 when Al (oxo)hydroxides starts to prevail (e.g., in bauxites) (Figure 4).
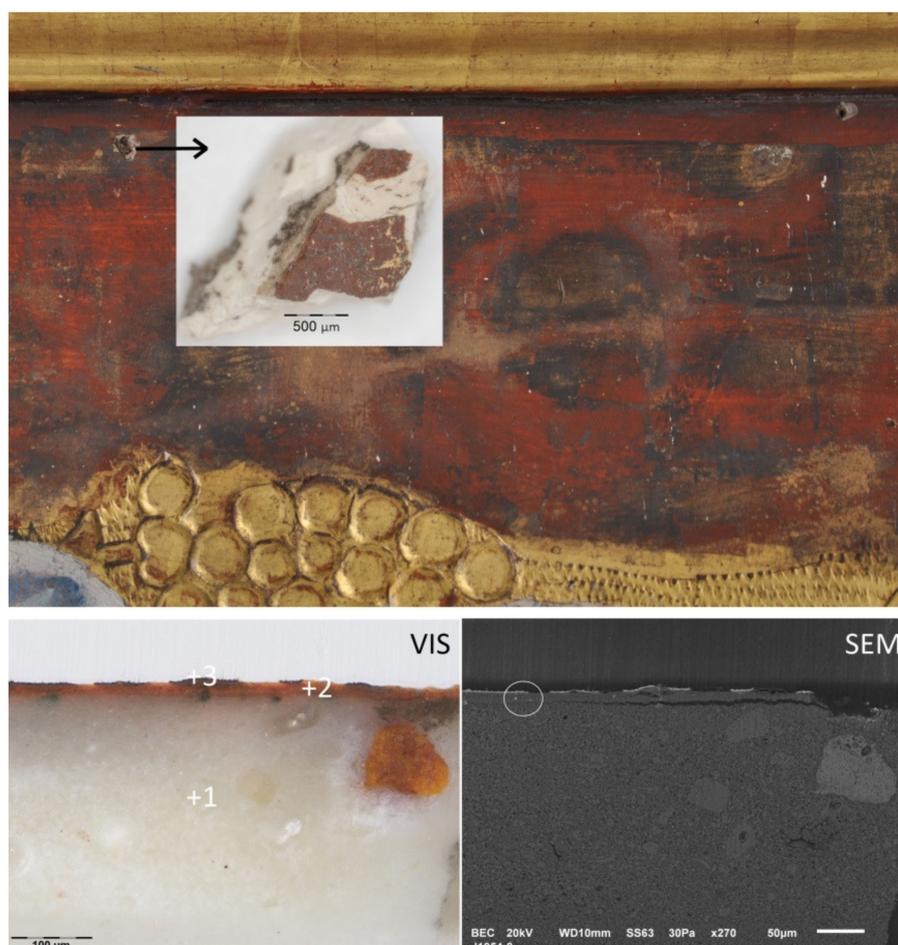
Figure 3. Late Gothic poliment on the St. George's altar (Spišská Sobota, Slovakia) dated before 1516, applied under the gilding (as visible in upper and lower parts of the macro-photograph) and under the *Zwischgold*, which is now highly degraded and detached from the surface (in the middle); an untreated fragment taken from a defect (indicated by arrow) was measured by powder X-ray micro-diffraction (micro-pXRD) from the top, because in the cross-section, the red poliment layer is too thin, as can be seen in visible light (VIS) or back-scattered electrons (SEM) images; +1 thick ground layer of natural chalk ($CaCO_3$) with an evidence of juvenile *Foraminifera* shells [38] and the proteinaceous isolation on the top; +2 poliment of a bauxite type (with gibbsite, boehmite, chlorite, micas, quartz, gypsum) additionally coloured by small grains of cinnabar (visible in the circle in the SEM image). (Photo of the Altar with permission from Miloš Fiľa, Slovak Monument Board; micro-photos obtained by Zeiss Axio Imager A.2 light microscope with the Olympus DP 74 digital camera for VIS, and by scanning electron microscope JEOL JSM6510 with detectors of back-scattered electrons for SEM, coupled with INCA EDS detecting unit to describe the elemental composition of individual layers and grains; photo with permission from Janka Hradilová and Silvie Švarcová; mineralogical analysis was performed on untreated fragment by PANalytical X'Pert PRO diffractometer equipped with a CoKα X-ray tube-point focus, X-ray mono-capillary with diameter of 0.1 mm and a multichannel detector X'Celerator with an anti-scatter shield).
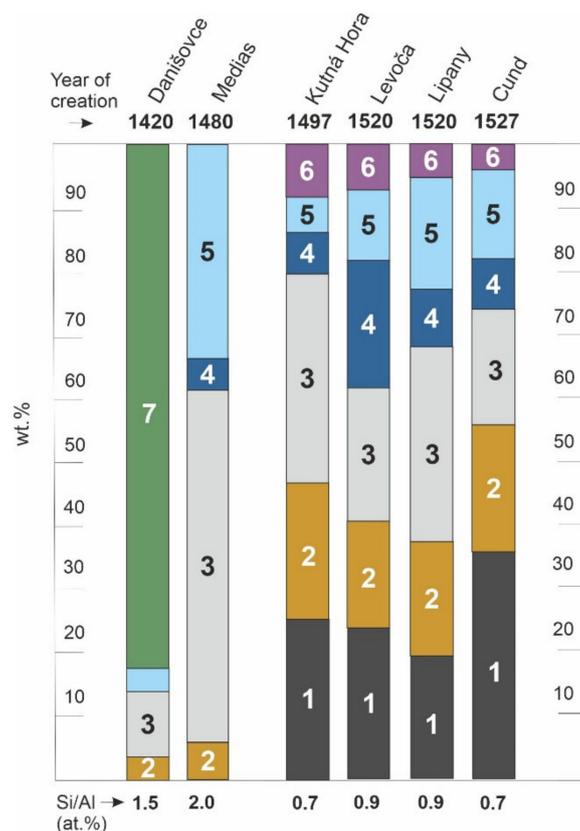
Figure 4. Si/Al ratios (bottom line) and representation of major phases in gilding/silvering poliments on selected East European artworks dated to the 15th and early 16th century, grouped to categories (according to [36]); 1—Al (oxo)hydroxides gibbsite and/or boehmite, 2—Fe and Ti oxides (hematite and anatase), 3,—kaolinite, 4—quartz, 5—mica group minerals, 6—chlorite group minerals, 7—expandable clay minerals; Danišovce = Mary Magdalene from Danišovce (polychromy on wood), Slovak National Museum—Spiš Museum, Levoča, Slovakia/Bohemian master; Mediaș = High Altarpiece (panel painting) of St. Margaret Evangelical Church from Mediaș, Transylvania, Romania/"Mediascher Meister" (Nurmberg?); Kutná Hora = Triptych "Death of the Virgin Mary" and predella (panel painting), Royal chapel, Italian Court at Kutná Hora/Kuttenberg, Czechia/unknown origin; Levoča = St. John Altar (panel paintings) at St. James Church in Levoča, Slovakia/Hans T.—workshop of Master Paul from Levoča; Lipany = Altarpiece of St. Martin (panel painting), Lipany, Slovakia/H.E.R., workshop of Master Paul from Levoča; Cund = Altarpiece of Saint Nicholas (panel painting), Ev. Church in Cund, Transylvania, Romania/Sighişoara Group of Workshops (according to [31], obtained by PANalytical X´Pert PRO diffractometer equipped with a CoKα X-ray tube-point focus + X-ray mono-capillary with diameter of 0.1 mm and a multichannel detector X'Celerator with an anti-scatter shield; Si/Al ratios calculated from JEOL JSM6510 SEM-EDS data).

It should be also mentioned that even earlier in the Middle Ages the composition of clay poliments varied significantly, which indicates different sources of import. Later in the Baroque period (e.g., [39]), it can be suggested that local/regional raw material sources start to prevail as the number of economically important mining sites of coloured clays in Europe was growing. In his famous book "Natural History of Fossils" from 1757, Emanuel Mendes da Costa [40] provides a list of boles of various origins (Bohemian, Hungarian, Silesian, French, English, German). Despite all of these facts, the term "Armenian bole" persists in many descriptions of gilding on actual artworks, simply because it "should be" by means of technology. Thus, the Armenian bole is an example of how the once established term can survive for centuries and gradually cover various materials of completely different origins. Since the original site of the supposed "montmorillonitic clay" in the former Armenia

has never been evidently found, it is not yet clear whether this ancient material is not a complete myth in European painting technology.

4. Bohemian Green Earth

The so-called "Bohemian green earth" represents a quite complicated mineralogical issue. In Europe, there were probably two main sources of the green earth pigment in Roman times—Verona in Italy and Smyrna (now Izmir) in Turkey. While the first location refers to celadonite found in the Late Eocene volcanites in the Monte Baldo area near Verona, Italy, the second location represents only the port, where the pigment was sold under the name 'Earth of Smyrna'. Its original location was the Massif of Troodos, in Cyprus [41]. Both these localities were exceptionally rich in blue-green celadonite and it resulted in a considerable spread of this pigment in Mediterranean and Italy. North of the Alps, there was a lack of cheap source of celadonite and therefore, other green pigments (as, e.g., copper-based pigments) were used more frequently. Since the Baroque, however, the largest Central European deposit of "celadonite" near Kadaň in Western Bohemia, Czechia, has gained in importance—the first mining galleries were opened in the 18th century [42,43].

It is not yet known to what extent this new pigment has been used in painting, since differentiating the green earths of various origins is not an easy task at the micro-scale. Individual green grains in paint layers are often too small for laboratory micro-pXRD and it is therefore advantageous to add spectroscopic micro-analysis with higher spatial resolution (as, e.g., micro-Raman and/or micro-FTIR). Micro-Raman can distinguish quite well between celadonites and glauconites [18,19], but it is not possible to differentiate celadonites by their origin. An important clue for recent research was that even in local Czech mineralogical literature, celadonite from Kadaň is often presented in quotation marks, what means that its mineralogical classification has never been definitively solved [44]. The colour of the Kadaň green earth also differed—it was rather grass green than blue-green, and the literature mentions a higher sorption capacity, which is considered to be advantageous in oil painting [45]. Since the 19th century, the popularity of the green earth from Kadaň highly increased and the pigment was exported as an industrial colour [46]. Variable colouring (from green to brown-green) indicates variations in the mineralogical composition, which is probably related to the fact that the sub-horizontal layer of hydrothermal celadonite at the contact of limnic limestones and basaltic tuffs was only 1–1.5 m thick and irregular. Rock samples from museums, old heaps and from the last accessible gallery minted at the beginning of the 20th century, are visually different.

It was found that the original Bohemian green earth was probably never pure celadonite. Although celadonite is present, the dominant phase in historical grass green samples is a regularly ordered interstratified mica/smectite structure of R3 type (Figure 5). Although glauconite/smectite R3 structure may also be considered, this is most likely a celadonite/smectite, as evidenced by the position of 060 diffraction line and the content of octahedral Fe^{3+} (not shown) [43]. In the last stages of mining of less valuable raw material, ferruginous smectite begins to prevail and celadonite is only locally found [47]. As the proportion of smectite increases, the colour changes to brown-green and the sorption capacity becomes higher. The accompanying phases are saponite, biotite, quartz, anatase, titanomagnetite, calcite and goethite (Appendix A). Although the R3 celadonite/smectite structure is a highly specific characteristic, it cannot be unequivocally proved in micro-samples. There is no way to apply specific clay science techniques, such as ethylene-glycol solvation, to such small and heterogeneous samples. However, it is possible to indicate the presence of smectite layers beside celadonite by micro-FTIR. It can be seen in Figure 6 that in the micro-sample taken from the local 18th century painting located in the Franciscan Monastery in Kadaň the characteristic region of FTIR spectra corresponds rather to the reference Bohemian green earth than to the pure celadonite from Monte Baldo near Verona, Italy. So far, Bohemian green earth has been indicated in this way in Baroque paintings in Western Bohemia, but also in paintings by the German painter Anton Kern (1709–1747) [43].
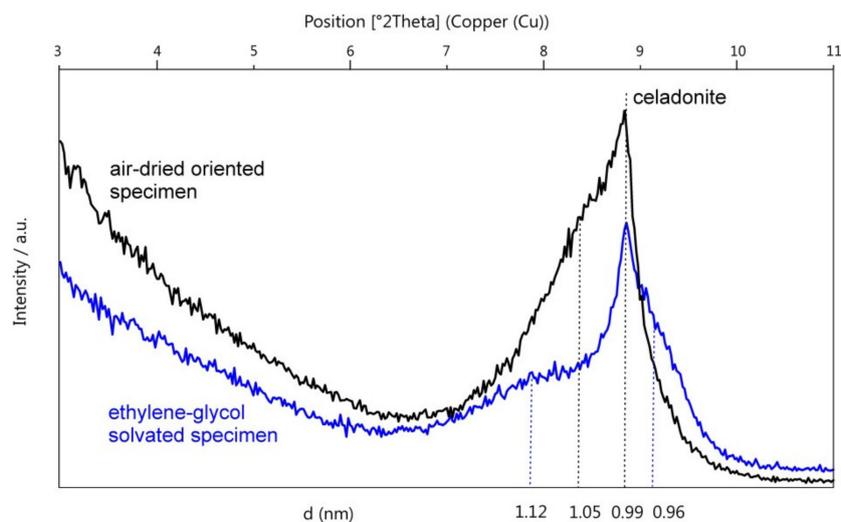
Figure 5. Evidence of interstratified mica/smectite of R3 type in the archival rock sample of Bohemian green earth from Kadaň area, Western Bohemia, as interpreted according to [24] and [43] from a comparison of diffraction patterns of air-dried and ethylene glycol solvated specimen; Diffraction line d(001) = 0.99 nm indicates mica (celadonite), while other diffractions represent the interstratified structure. (Obtained by Siemens D-5005, Bruker with CuKα radiation, a secondary monochromator and a common scintillation detector).
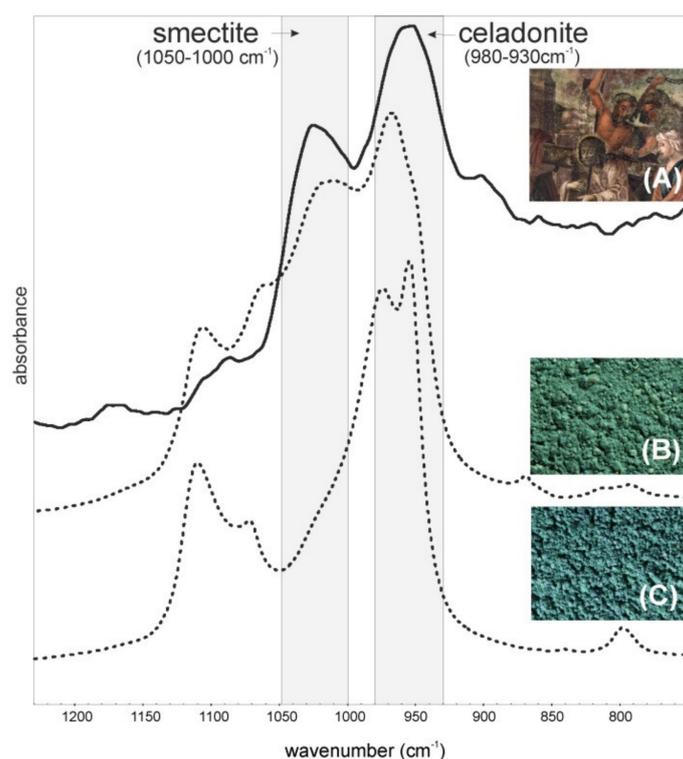
Figure 6. Micro-FTIR spectra of green earth grains found in oil-on-canvas painting from Calvary Cycle located in the Franciscan Monastery at Kadaň, Czech Republic, dated to the 18th century (**A**) in comparison with reference spectra of Bohemian green earth (Úhošťany near Kadaň, Czech Republic), representing interstratified celadonite/smectite (**B**) and Verona green earth (Monte Baldo near Verona, Italy) representing pure celadonite (**C**) (According to [43]; obtained by Nicolet Magna 750 FTIR spectrometer at a resolution of 4 cm^{-1} for rock samples and by Continuum infrared microscope with a Nicolet Nexus micro-spectrometer, Thermo Fisher Scientific Inc., Waltham, MA, USA, at resolution of 4 or 8 cm^{-1} for the microsample; the spectra were recorded in the region 4000–650 cm^{-1}).

However, it is necessary to always consider the timeline, current terminology, and historical point of view in provenance studies. In conclusion, therefore, we can note that recently commercially available Verona green earth is brownish-green and contains mostly smectite, as the celadonite from this source is almost exhausted (similarly to Kadaň a hundred years ago) and that under the name "Bohemian green earth" light green glauconites from Prague area are provided by commercial suppliers. Not in all cases these facts are considered even in recent comparative studies [48].

5. Provenance of White and Red Earths

Natural kaolin has always been the most important source of white earth. It is generally assumed that due to the high availability, sources were only local or regional. In Gothic wall paintings in St. Maria Magdalena Church in Bor near Karlovy Vary, western Bohemia, kaolin was found in the preparatory layer, where it partly substituted a limewash [26]. Because the church is located in a region with significant kaolin deposits [49], it looked from the beginning more like a casual use of locally available material than as a targeted technological change—despite the fact that the extensive mining of these kaolins has started much later in response to the porcelain production development in the 18th century. In order to prove this suggestion, laboratory micro-pXRD was combined with synchrotron radiation XRD (SR-XRD) and the crystallinity indices of kaolinite were calculated as Hinckley indices (HI [50]) and AGFI indices [51]. (HI is calculated conventionally as a sum of (1-10) and (11-1) peak heights measured from the heel of peaks divided by (11-1) peak height measured from the background of the diffraction pattern. AGFI is calculated as a sum of (1-10) and (11-1) peak heights divided by double 020 peak height determined after peak decomposition procedure. Kaolins from all important locations in the Czech Republic were included to this comparative study. Regardless of whether the indices were calculated as Hinckley or AGFI indices, it was confirmed that the crystallinity of kaolinite in the painting (HI = 1.10; AGFI = 0.74) perfectly corresponds to the crystallinity of local kaolinite from Karlovy Vary area (HI = 1.01; AGFI = 0.74). Since other Czech kaolinites were better ordered (HI = 1.39–1.61; AGFI = 1.04–1.51) it was possible to determine that the kaolin used was locally extracted—possibly directly from the church's subsoil [26].

If the regional provenance of the earth pigment cannot be directly determined from the material characteristics, the knowledge of the historical context is necessary for a correct interpretation. It was found, for example, that Master Paul from Levoča, Slovakia, who is considered to be one of the leading artists of late Gothic art in Central Europe, intentionally admixed kaolin to chalk grounds on some of his altars located in Northern Slovakia (Figure 7, [38]) Based on the presence of alunite (evidenced by micro-pXRD and micro-Raman techniques) accompanied by kaolinite, quartz, and opaline silica, the kaolin was specified as hydrothermal (Figure 8, [52]). Since mineralogical analysis did not show any characteristics that would lead to the determination of provenance, historical consequences were considered in order to indicate the place of origin of this unusual material. At the time of artworks' creation Slovakia was an integral part of the Kingdom of Hungary; the municipality of Levoča traded with Tokaj wine and also owned vineyards in the Tokaj area [53], where the hydrothermal kaolin's quarries are located and mined until the present days. Although there are other possible sources in Slovakia the region of the Tokaj Mountains thus seems to be very probable because of its significance and availability through the trade routes.
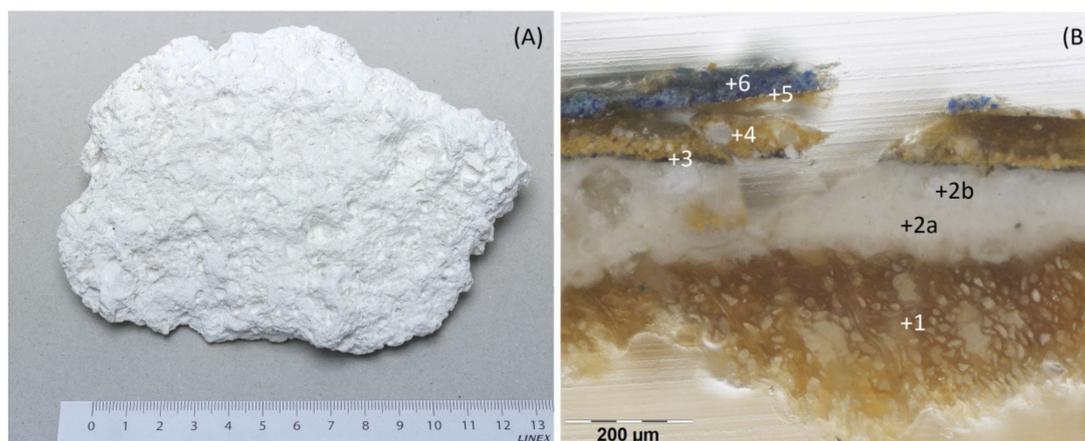
Figure 7. Reference sample of hydrothermal kaolin from Király Hill, Tokaj Mts., Hungary (**A**); this or similar material was admixed to the bottom ground layer—indicated as +2a in the sample cross-section (**B**) of the polychrome statue of St. John the Baptist from the St Johns' altar at the St. James church in Levoča, Slovakia, dated to around 1520, attributed to Master Paul from Levoča; +1 wooden support, +2 chalk-based ground with admixtures of kaolin in the bottom layer (+2a), +3 underdrawing, +4 "mordant" preparation layer for oil gilding, +5 gold foil, +6 overlay of blue drapery (according to [38] and [52], obtained by Zeiss Axio Imager A.2 light microscope with the Olympus DP 74 digital camera, micro-photo with permission from Janka Hradilová).
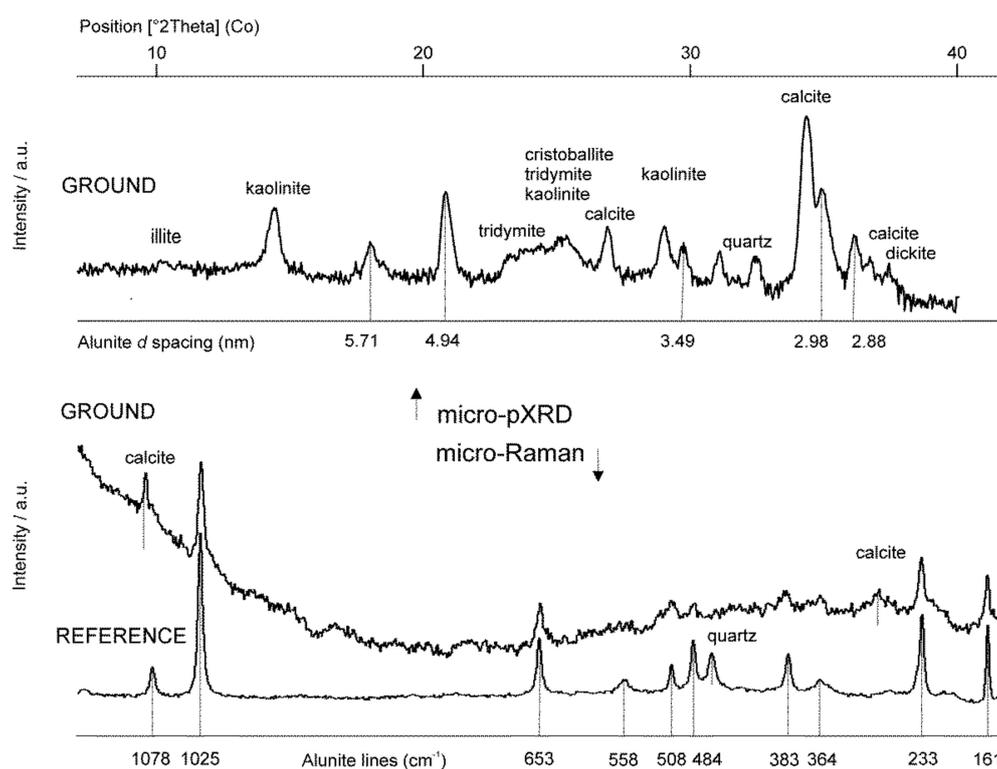
Figure 8. Characteristic lines of alunite in micro-pXRD diffraction pattern (**top**) and micro-Raman spectra (**bottom**) of the ground layer, which proves a hydrothermal origin of kaolin admixed to chalk grounds by Master Paul from Levoča (see Figure 7) (according to [52], obtained by PANalytical X'Pert PRO diffractometer equipped with a CoKα X-ray tube-point focus, X-ray mono-capillary with diameter of 0.1 mm and a multichannel detector X'Celerator with an anti-scatter shield, and by ThermoScientific DXR Raman Microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA), single mode diode laser 780 nm, interfaced to an Olympus microscope (Olympus, Tokyo, Japan) in the 30–1870 cm^{-1} spectral region with a resolution of approximately 2 cm^{-1}).

Another example of the consistency of historical and analytical data can be seen in the paintings by Johann Georg de Hamilton (1672–1737), who came from a Scottish family and learned to paint in the Netherlands, but spent a large part of his productive life in Vienna in the service of Schwarzenbergs [54]. His portraits of horses from the Schwarzenberg stables and other natural scenes, which he painted not only in Austria but also in Southern Bohemia, exhibit the Netherlandish painting technique (Figure 9). However, the composition of the ground (= priming layer applied directly on the canvas/wood support) differs. The red earth used has an unspecific composition with only kaolinite, illite, quartz, and hematite. Although such materials can be found in many places in Europe, the archive data direct us to Bavaria, where Hamilton allegedly bought already primed (= coated with ground) canvases (Schwarzenberg family's archive, deposited in the National Regional Archive in Třeboň, Czech Republic). Indeed, in Bavaria there is a significant and still-available red earth deposit near Troschenreuth—and the reference material available today (known as "German bole") has the same mineralogical composition. In order to prove this suggestion quantitative micro-pXRD analysis [25] and, as a part of a methodological testing, also trace element analysis (LA-ICP-MS) had been performed [29]. Figure 10 shows a very good match in the composition of the Hamilton's red ground and the German bole from Troschenreuth in most of the analysed chemical elements. Larger deviations can be seen only in the contents of some elements, such as, e.g., Zr or Hf. Contrarily to the reference red earth, the artwork sample was characterized by significantly increased values of Pb and Sb (>10 times, not included in the graph), which may indicate the presence of some Pb-based pigments intentionally added directly to the ground layer, which was not an uncommon phenomenon in the Baroque period. The possibility of accidental contamination during the canvas priming, e.g., by dirty brushes, also has to be taken into account. One can speculatively imagine that also concentrations of Cu (indicating some Cu-based pigments), or even Ca and P (indicating the bone ash) can be artificially affected. Despite these partial differences, it was satisfactorily proved that the material for Hamilton's ground was mined in Troschenreuth, Bavaria.
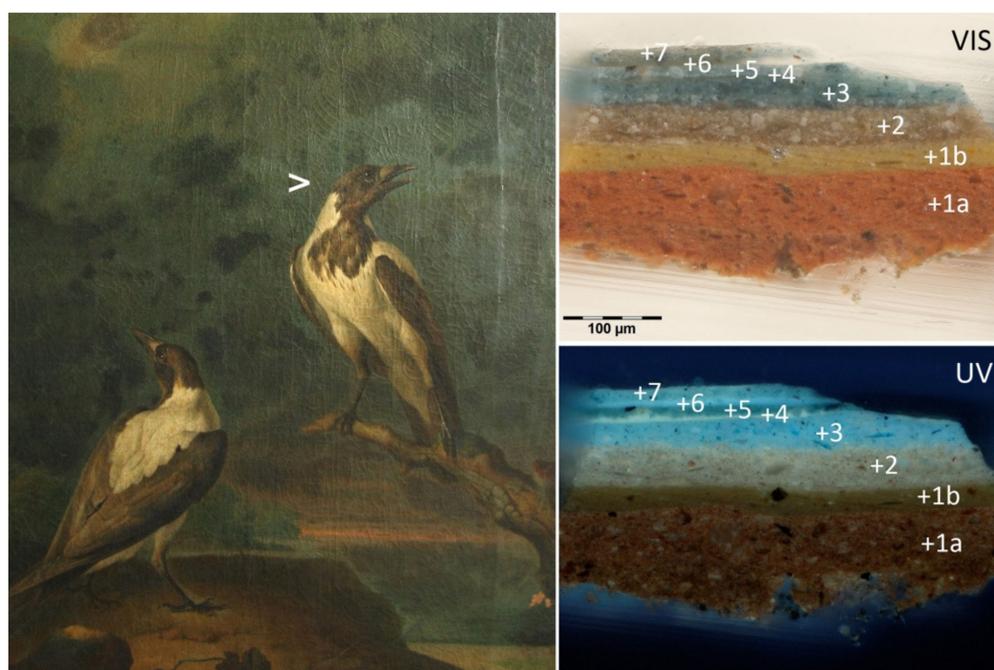
Figure 9. Detail from oil-on-canvas painting by Johann Georg de Hamilton *Two Hooded Grous* dated to 1729, Czech Monument Board České Budějovice, Castle Hluboká, with the indication of the sampling location (**left**) and micro-section from the blue background in VIS and UV light (**right**); +1 double

layered red/yellow clay based ground containing common earths with quartz, kaolinite, illite and hematite or goethite, +2 lead white slightly coloured by earth pigments, +3 original paint by lead white and Prussian blue (Appendix B), +4 isolation layer, +5 overpaint by lead white and Prussian blue, +6 isolation layer, +7 overpaint by lead white and Prussian blue (Photo with permission by Olga Trmalová, before restoration, micro-photos in VIS and UV—365 nm lights obtained by Zeiss Axio Imager A.2 light microscope with the Olympus DP 74 digital camera and Colibri 2 fluorescence module, with permission by Janka Hradilová; scanning electron microscope JEOL JSM6510 with detectors of back-scattered electrons INCA EDS detecting unit was used to describe the elemental composition of individual layers and grains; mineralogical analysis of the ground was performed on untreated fragment by PANalytical X´Pert PRO diffractometer equipped with a CoKα X-ray tube-point focus, X-ray mono-capillary with diameter of 0.1 mm and a multichannel detector X'Celerator with an anti-scatter shield).
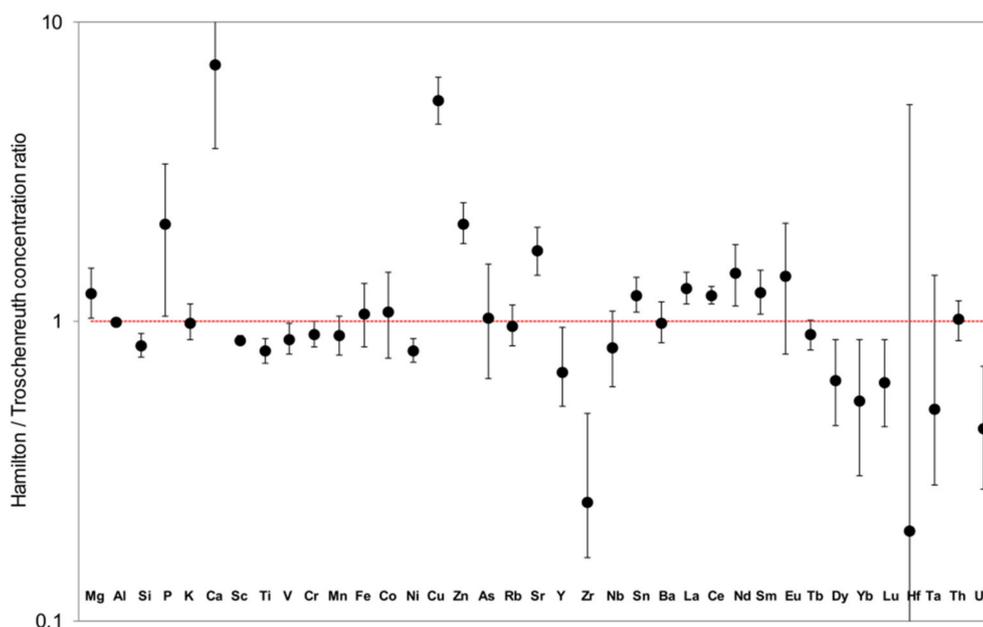
Figure 10. Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) concentration ratio of the red-orange ground by Hamilton and reference red earth sample from historical source in Troschenreuth, Bavaria, including the value range (lines, calculated from standard deviations) (according to [29], obtained by 7900 ICP-MS analyser, Agilent Technologies, Santa Clara, CA, USA, line scan ablation-1200 × 110/85 μm eliminating the sample inhomogeneity).

6. From Pottery to Painting

In the Baroque period, clay-based priming layers (grounds) were applied on canvas in all parts of Europe (instead of previously used chalk or gypsum—"gesso"). Similarly, as in the case of poliments (see Section 3), they have been sometimes incorrectly referred to as "bole grounds", although they were represented by clay materials of very different compositions and origins. There are two questions arising. Could the composition of clay-based grounds correspond to the place of an artwork creation (regarding the common practice in that time that painters preferred to buy already primed canvases in places, where they were working, as for Hamilton)? And where did this significant technological change (i.e., replacing white grounds with coloured clays) begin and why? In order to answer the first question, it is necessary to compare the mineralogical compositions of clay-based grounds of different regional provenances. It can be confirmed, for example, that there are significant differences between Italian and Central European grounds of the turn of 17th and 18th centuries [28].

Even within one wider region (as, e.g., the Central Europe), we encounter more than one economically important locality. Instead of red earth from the Bavarian Troschenreuth (mentioned in the previous chapter), some painters preferred a high-quality red clay from the West-Bohemian

town of Hořenec—for example the prominent Czech Baroque painter Karel Škréta (1610–1674) [55]. This clay consisted only of kaolinite, hematite and anatase, and because of almost negligible content of quartz, it corresponded very well to the definition of the "bole". However, among all the Baroque grounds this is rather an exception. Even when using a wider term "earthy grounds" instead of "bole grounds", when speaking about the Baroque grounds in general, it can be misleading. The composition of the first ever coloured grounds, which appeared in Italy in the turn of 16th and 17th century and which were extensively used by North-Italian painters like Caravaggio (1571–1610) [56–58] and his followers [59], did not correspond to any earth pigment exploited in Italy (despite the fact that there are numerous traditional areas of ochre mining—such as Lessinnian Mountains [60] or Mt Amiata area near Siena [61]). Thanks to the contents of quartz, mica, chlorite, and feldspars, but also a considerable amount of calcite and, eventually, also dolomite (Appendix A), this material can instead be classified as calcareous clay. One of the highly specific features is the presence of framboidal pyrite (Appendix A, Figure 11), which indicates reductive conditions in the sedimentary basin.
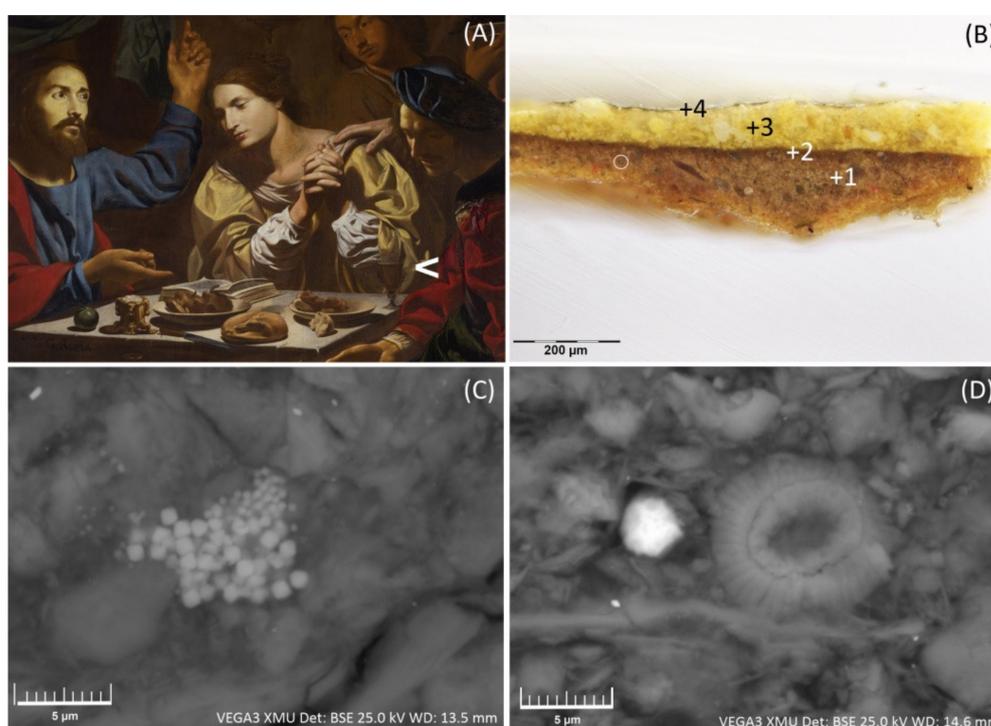
Figure 11. Detail from oil-on-canvas painting by L.G. Roma *Christ in the House of Maria and Martha*, dated to the 17th century, Slovak National Museum-Historical Museum, Bratislava Castle, Slovakia, with the indication of the sampling location (**A**), which is painted on the clay-based ground (**B**), classified as calcareous pottery clay; +1 pottery clay—with chlorite, illite, quartz, feldspar, calcite and dolomite), additionally coloured, e.g., by hematite (red grains), +2 thin brush underdrawing, +3 oil paint by lead-tin yellow, +4 varnish; at high magnification in the scanning electron microscope image (**C,D**), the characteristic details of this material are highlighted—the presence of framboidal pyrite (**C**), which appears in the cross section (**B**) in the middle of the ring, and micro and nano fossils (**D**), which help to determine the age of the material to late Eocene-Oligocene. (Photo Archive of the SNM-Historical Museum Bratislava, micro-photos obtained by Zeiss Axio Imager A.2 light microscope with the Olympus DP 74 digital camera and by scanning electron microscope (SEM) TESCAN VEGA 3 XMU (TESCAN ORSAY HOLDING, a.s., Brno, Czech Republic) equipped with a detector of back-scattered electrons, coupled with INCA EDS detecting unit to describe the elemental composition of individual layers and grains; photo with permission by Janka Hradilová and Zuzana Korbelová; mineralogical analysis of the ground was performed on untreated fragment by PANalytical X´Pert PRO diffractometer equipped with a CoKα X-ray tube-point focus, X-ray mono-capillary with diameter of 0.1 mm and a multichannel detector X'Celerator with an anti-scatter shield).

Surprisingly, a material of exactly the same mineralogical composition was also used by sculptors, as was confirmed by the analysis of one unfired clay (terracotta) statuette of Bologna or Florence provenance dated to the turn of the 16th and 17th century [30]. It allows us to conclude that the ground material is pottery clay in fact, and its cheap availability in northern Italy at that time would be related to the increased popularity of terracotta sculptures, which started during the Renaissance, and to the subsequent expansion of pottery clay mining. Speculatively, one can assume that it was legally this cheap availability that led someone (perhaps Caravaggio himself) to apply this new material as for the ground of canvas painting in order to darken the painting and to achieve a strong contrast between light and dark, which is known as *chiaroscuro* [58]. This could also be the answer to the second question raised in the introduction of this chapter. It is a nice example of technological transfer, when the material originally mined for other purpose (ceramics, sculptures) was secondarily used in another branch (here in painting). This was economically advantageous in spite of the fact that the dull grey-beige colour of the clay had to be additionally improved with added pigments to the final brown-red hue. (Figure 11)

Pottery clays are found in many places in Europe, but if one assumes an Italian origin, the range of possible sites is shrinking. Mineralogical clues, however, are not sufficient to determine the historical mining location. In this particular case, it was an advantage that the clays contained significant calcareous component rich in micro- and nannofossils. Although it was possible to separate only a small amount of material (in micrograms) from the ground layer for the micro-palaeontological description of nannoplankton, it was possible to determine the geological age of the clay to Late Eocene–Oligocene [30]. Considering this finding, two possible areas of origin of these clays had been pre-selected. The Ranzano Formation at Sassuolo district (Emilia Romagna) was suggested to be the best candidate not only because of conformity of the geological age (Middle Eocene–Early Oligocene) and mineralogical and chemical composition, but also because of a long-term tradition of the clay exploitation and use for ceramic tiles, which is widely documented [62]. The production of bricks and ceramic tiles in this region was known already in the 17th century. [63] The second candidate unit was Macigno Formation (Tuscan Nappe), which is formed by lithologically suitable rocks of Oligocene-Miocene age. Within preliminary investigation rock samples have been collected in active and abandoned quarries near Sassuolo (Ranzano Formation) and in several outcrops in the Florence vicinity (Macigno Formation). According to still-preliminary results, the composition of grounds from the paintings of Italian Caravaggists better matches the samples from Sassuolo - mineralogically, palaeontologically and chemically (including trace elements) (Figure 12). Samples of Macigno Formation from Florence area were found to be poor in carbonate and fossil contents and although this component may vary significantly place to place, the difference in trace element contents serve as another argument.

Art historians often believe that the changes in the composition of the materials are solely related to the invention of the painter. This is only partially true. Painters were improving the grounds (additional colouring, re-priming = adding a new layer of different colour). The basic material, however, was locally available raw material. Matia Pretti (1613–1699) used pottery clays in paintings created in Italy, while weathered reddish *Globigerina* limestones were used instead of clays in his paintings created in Malta. Their local origin was again confirmed by both mineralogical and paleontological data. [64] Also the ground of one of the latest paintings by Caravaggio created in Malta (*Beheading of St. john the Baptist*, Valetta Cathedral) differs from all the previous ones. The dominant components in this case are alunite and hematite, and although the source of this material in the Mediterranean is not yet known, it again represents a very specific composition [64].
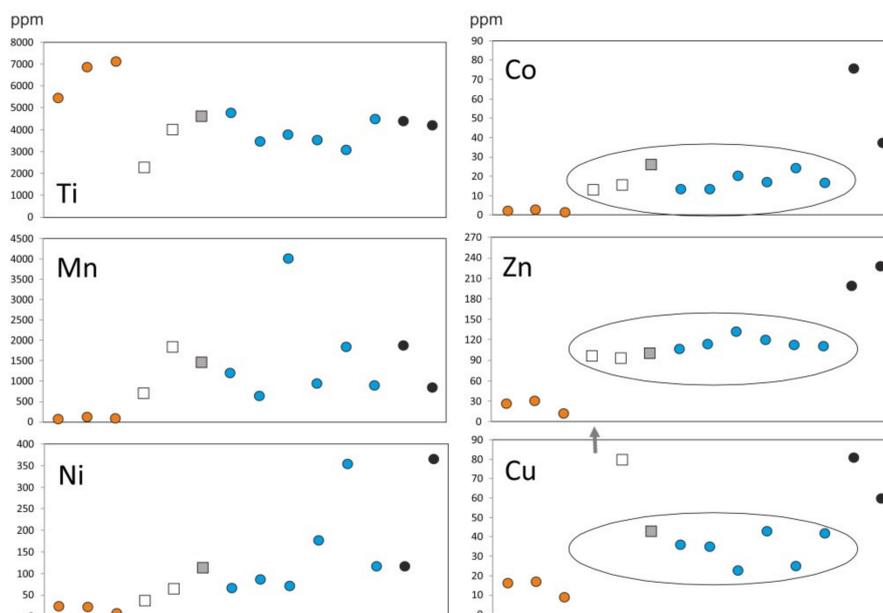
Figure 12. Preliminary results of a comparative LA-ICP-MS analysis (selected elements) performed on grounds of Italian 17th century paintings (open squares), one unfired terracotta sculpture of Italian provenance (grey square), reference pottery clays from Sassuolo district (Ranzano Formation, Oligocene, blue circles) and clay rocks at Florence area (Macigno Formation, Oligocene–Miocene, black circles); for comparison, a composition of red earths from two significant Central European locations in Bohemia and Bavaria was included (orange circles); while Ti, Mn or Ni can be used to distinguish Italian and Central-European sources, Co, Zn and Cu look very promising to differentiate source areas in Italy (however, contamination with other pigments in the layer must be avoided, which in this case was not possible with Cu). (obtained by 7900 ICP-MS analyser, Agilent Technologies, Santa Clara, CA, USA, line scan ablation-1200 × 110/85 μm eliminating the sample inhomogeneity).

7. Conclusions

In recent years, non-invasive instrumental techniques have been developed very rapidly, allowing paintings to be studied in-situ (using mobile devices) or ex-situ, but without the need to take a sample. Although the amount of information gathered in this way is increasing, the provenance analysis of the materials used is still an example of such a complicated question that cannot be solved without "touching" a painting. The term "provenance analysis" is usually understood to be the search for such materials/technological characteristics that help to refine dating, painter, or workshop attribution, or also the place of the painting's creation. Therefore, valuable scientific data are still not provided to support art-historical consideration when using non-invasive techniques only.

As can be seen from the case studies presented here, in addition to cutting-edge micro-analytical instrumentation, very good contextual knowledge is also needed in order to effectively link analytical measurements of samples with the understanding of historical art technology, sources and technologies of painting materials' production and the ways of economical thinking in the past. The example of clay minerals in earthy pigments, which were discovered for the purpose of provenance studies only recently, also showed how important is the application of mineralogical and geological approaches in the analysis of historical art.

In many cases, these approaches favour diffraction methods, which are still less frequent in the practice of fine arts' analysis than, e.g., spectroscopic methods. For the microanalysis of clay minerals in paints, the powder X-ray micro-diffraction method has proven to be absolutely essential and indispensable, although it is further combined with trace element analysis, micro-palaeonotological analysis or with spectroscopies (micro-FTIR, micro-Raman).

Thanks to detailed analysis, it has been shown that traditional and frequently repeated terms often change their actual content—the Bohemian green earth was formerly interstratified celadonite/smectite, and in the recent production it is glauconite. The "Armenian bole" may not have existed in European gilding technology at all, and the composition of the gilding poliments illustrates the use of various materials—not only clays, but also bauxites. The term "earth", which is traditionally used for any alumosilicates in preparatory and painting layers, is sometimes unsuitable for Baroque painting grounds, since Italian artists (starting with Caravaggio) did not have any earth available—they used cheap pottery clay and additionally they modified its colour. In the Baroque, the regional specificity of the priming layers (grounds) is clearly documented. While in northern Italy canvases were primed with pottery clay, weathered *Globigerina* limestones of local origin were used on Malta Island. The grounds of paintings by one single artist thus differ according to the place where the painting was created. Isn't this a good and promising finding for the provenance analysis of anonymous works?

Appendix A

Table A1. List of Minerals/Group of Minerals Mentioned in the Text.

Clay Minerals—Fine-Grained Phyllosilicates	
celadonite	$K(Mg,Fe^{2+})Fe^{3+}(Si_4O_{10})(OH)_2$
dickite (polytype of kaolinite)	$Al_2Si_2O_5(OH)_8$
glauconite	$(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$
chlorite	group of clay minerals, e.g., clinochlore $Mg_5Al(AlSi_3O_{10})(OH)_8$
illite	$K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$
kaolinite	$Al_2Si_2O_5(OH)_8$
montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$
saponite	$Ca_{0.25}(Mg,Fe)_3((Si,Al)_4O_{10})(OH)_2 \cdot nH_2O$
smectite	group of expandable clay minerals, e.g., montmorillonite or saponite
palygorskite	$(Mg,Al)_5(Si,Al)_8O_{20}(OH)_2 \cdot 8H_2O$
Other Minerals	
aerinite	$(Ca,Na)_6Fe^{3+}Al(Fe^{2+},Mg)_2(Al,Mg)_6[Si_{12}O_{36}(OH)_{12}H][(H_2O)_{12}(CO_3)]$
anatase	TiO_2
biotite	$K(Fe^{2+}/Mg)_2(Al/Fe^{3+}/Mg)([Si/Al]Si_2O_{10})(OH/F)_2$

Table A1. *Cont.*

Clay Minerals—Fine-Grained Phyllosilicates	
boehmite	γ-AlO(OH)
calcite	$CaCO_3$
cinnabar	HgS
cristoballite (constituent of opal)	SiO_2
dolomite	$CaMg(CO_3)_2$
feldspar	group of tectosilicate minerals, e.g., orthoclase $K(AlSi_3O_8)$
gibbsite	γ-Al(OH)$_3$
goethite	α-FeOOH
gypsum	$CaSO_4 \cdot 2H_2O$
hematite	Fe_2O_3
jarosite	$KFe^{3+}{}_3(SO_4)_2(OH)_6$
mica	group of phyllosilicate minerals, e,g, muscovite or illite (clay-sized)
pyrite	FeS_2
quartz	SiO_2
titanomagnetite	$Fe^{2+}(Fe^{3+},Ti)_2O_4$
tridymite (constituent of opal)	SiO_2

Appendix B

Table A2. List of Artificially Prepared Pigments Mentioned in the Text.

Name	Formula and Explanation
lead-tin yellow	Pb_2SnO_4 (type I), $Pb(Sn,Si)O_3$ (type II)
lead white	$2PbCO_3 \cdot Pb(OH)_2$ (equivalent of mineral hydrocerussite)
massicot	PbO (equivalent of natural massicot)
Naples yellow	$Pb_2Sb_2O_7$ (equivalent of mineral bindheimite)
Prussian blue	$Fe^{3+}{}_4[Fe^{2+}(CN)_6]_3$
Maya blue	Complex of plant dye indigo and palygorskite-$(Mg,Al)_5(Si,Al)_8O_{20}(OH)_2.8H_2O$

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