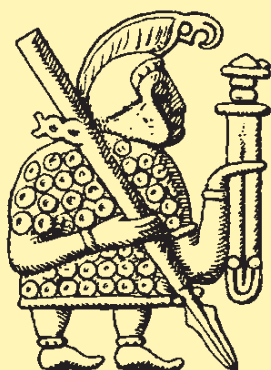


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Pigments used in medieval Scandinavia – types, origin, trading routes

By *Anders G. Nord and Kate Tronner*

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In ancient times, Scandinavia was a remote part of Europe. However, the Vikings travelled by boat as far as the Mediterranean Sea and brought home various pigments to paint their runic stones. The Middle Ages (around 1000–1500 AD) witnessed a large import of pigments for the Church, used to decorate murals, wood sculptures, baptismal fonts, and portals. The authors have analysed 993 samples of medieval pigments from Sweden. Most results have been published in Swedish, though. We now make an attempt to comprise the data and compare it with analytical results from Denmark, Norway and some European countries.

Lead isotope data and secondary minerals have helped to attribute pigments to specific regions. Germany seems to have been the most important trading partner, in particular as regards pigments containing copper or lead. Rare mineral pigments from distant countries, such as cinnabar, orpiment, gold and even ultramarine, were probably obtained from trading companies within the Hanseatic League. This union was for many centuries active in the Baltic Sea and North Sea coastal areas, where Scandinavia was represented by towns like Copenhagen, Roskilde, Bergen, Kalmar, Visby and Stockholm.

Keywords: Medieval pigments, Scandinavia, analysis, transformation, origin

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Introduction

It is well known that mineral pigments were used all over the world, probably more than 20 000 years ago, to decorate outdoor rocks or caves. Later, Scandinavian Vikings travelled by boat to south Europe and brought home various pigments to paint their runic stones, and some analytical data are available. The Middle Ages began around 1000 AD in Denmark, somewhat later in Sweden and Norway. Small churches were first built in south Scandinavia, several centuries later in the northernmost regions. With time, the original small churches were replaced

by larger buildings. Almost all medieval Danish churches were built of stone. Even in Sweden stone churches dominated, but in Norway most medieval churches were built of wood. Monasteries were also erected, today most of them in ruins. Many of the stone churches were internally decorated with murals, and sometimes also their baptismal fonts, stone portals and sculptures were painted using various pigments. In some cases, it has been possible to determine the origin of pigments by use of lead isotopes or secondary minerals in the mineral pigments,

as will be exemplified below. Knowledge about colour changes among the pigments is essential. Foreign influence, origin and trading routes are discussed. The need for chemical analyses of the pigments is obvious for conservators and art historians working with old paintings.

Analytical methods

All Swedish samples were carefully sampled, afterwards examined with an optical microscope and analysed by SEM/EDX. Sometimes additional techniques were used such X-ray powder diffraction (XPD) or X-ray fluorescence (XRF). In rare cases we utilized a polarization microscope. For organic colorants or organic binding media, FTIR and/or GC-MS was used. To determine the lead isotope composition, an MC-ICP-MS spectrometer was utilized. The Danish and Norwegian material was examined with similar methods. Many of the Danish murals were in fact analysed by in situ X-ray fluorescence, a gentle method because no samples had to be taken.

Medieval pigments: Sweden

From the Middle Ages, there are thousands of paintings in the Scandinavian churches. The medieval Scandinavian material so far analysed is incontrovertibly largest for Sweden. As many as 993 samples of pigments have now been analysed by the authors within a period of thirty years. In addition, about 40 other samples from murals have been reported by other authors, and paint from wooden sculptures have been analysed by our former colleague Peter Tångeberg (1970; 1984; 1993; 2020). Our first publication appeared in 1996 (Nord et al. 1996). Most other results have been published in *Fornvännen* (mainly in Swedish) or in *Studies in Conservation*. Besides, we have published results in *Journal of Cultural Heritage*, at international conferences, or in reports published by the National Heritage Board of Sweden.

About 500 churches with at least some medieval paintings are preserved in Sweden, and from 70 of these the authors and their colleagues have collected samples of pigments. Most material has been obtained from wealthier regions such as south Sweden, the Mälaren surroundings and

the island Gotland in the Baltic Sea. The examined paintings date from about 1100 A.D. to 1550 A.D. The medieval Church farthest north is situated near the Arctic circle: Nederluleå church. It is now inscribed in the UNESCO World Heritage List. In each church, we tried to restrict the sampling to a few representative paintings. In churches under conservation, many samples could be collected. We always endeavored to obtain samples of all colours and shades, reflecting the palette of the painter. However, for various reasons this could not always be achieved. From some churches we were given just a few samples by a conservator or art historian, interested in a specific problem. Accordingly, the number of samples from each church varies between 1 and 78 (average: 14). About 300 samples originate from murals created by the renowned master Albertus Pictor (†1509), a German by birth (Nord et al. 2018).

As regards our own material, 906 samples were taken from *a secco* murals. The binding medium was always lime; in rare cases we also encountered traces of drying oils or proteins. In addition, 26 samples were collected from 12th century Byzantine paintings on wood panels from since long demolished stave churches (Nord et al. 2017). Another 44 samples were taken from baptismal fonts of stone (Nord et al. 2016), and 17 from outdoor portals (Nord & Trønner 2014). Besides, one of the authors' former colleagues, Peter Tångeberg, has devoted half his life to the study of paint on religious sculptures of wood (cf. next section).

For the convenience of the reader, the data for medieval Swedish paintings are comprised in Table 1. Natural minerals as well as synthetic pigments are included. During the Middle Ages, many pigments were produced on the European Continent in glass works and smelting-works such as lead pigments, smalt (cobalt glass), and Naples' yellow, a lead antimonate. Among the natural minerals, the following have been found: lime, chalk, gypsum, iron oxide/hydroxide, yellow ochre, red ochres, umber, green earth, malachite, atacamite, azurite, cinnabar (HgS), orpiment (an arsenic sulfide), blue and green vivianite, and ultramarine. For black, carbon black (soot) was practically always used. The

synthetic pigments found were minium, lead monoxide, lead tin yellow, lead white, atacamite (cf. below), and Naple's yellow. We also found some organic colorants such as Brazilin. For detailed information of each pigment, we refer to Howard (2003). Many of the lead pigments have oxidized with time (cf. below). It should also be mentioned that in about every third church, we encountered pigments from the last two hundred years such as copper arsenite, chromium oxide, viridian, barium sulphate, zinc white, and/or titanium dioxide. This indicates that they were used for restoration during the last two centuries, something which is not allowed today. For some reason, chromium oxide and barium sulphate were quite often found together.

Paint from Swedish wood sculptures have been analysed by one of our former colleagues, Peter Tångeberg (1970; 1984; 1997; 2020). The pigments used agree with those summarized in Table 1, with some distinct deviations. For instance, the use of gold was quite common on the wood sculptures; also silver and tin had been used. For green colour, the synthetic pigment verdigris, a copper acetate, was usually used.

Verdigris is stable on wood but not on a ground of lime.

Medieval pigments: Denmark and Norway

When Christianity had been adopted in Denmark, around 1 700 churches were built, almost all of stone. Many of them were decorated with murals. Only a small number of their murals have been analysed with respect to their pigments. Also some sacred wood sculptures have been examined and their paint analysed. In the Danish murals, the same pigments were used as for the Swedish murals (tab. 1), with some differences (Christensen 2020; Taube 2020; Trampedach 2020). For instance, malachite is rare in Danish murals, although it is very common in medieval Swedish murals. On the other hand, atacamite [$\text{Cu}_2\text{Cl}(\text{OH})_2$] is often observed in the Danish murals, a fact which will be argued in the Discussion section (below). Furthermore, lead monoxide (PbO) and green earth are rare in the Danish medieval murals, while smalt and even gold sometimes have been identified in wall paintings. These differences are certainly interesting. Also paint on Danish wooden ob-

Occurrence	Mineral pigments	Synthetic and other pigments	Transformed pigments
<i>Very common</i> (almost always found)	Carbon black, lime (CaCO_3), Iron oxide/hydroxide		
<i>Common</i> (identified in about 50% of the churches)	Yellow ochre, malachite, atacamite, azurite, gypsum	Minium (Pb_3O_4) (Probably also Atacamite may have been synthesized)	Plattnerite ($\beta\text{-PbO}_2$)
<i>Less common</i> (found in about 10 churches)	Cinnabar Ultramarine Green earth Vivianite Volborthite (a yellow secondary mineral found in malachite) Caput mortuum Red ochre Orpiment Umber	Lead monoxide, PbO Lead tin yellow Lead white	
<i>Rare</i> (1–3 churches)	Gold (on baptismal stone fonts)	Smalt Naple's yellow Brazilin red (organic colorant from the Brazilwood tree) Indigo	Metacinnabarite (black HgS) Tenorite (black CuO)

Tab. 1. Summary of the pigments found in medieval church paintings in Sweden (paint on stone). The data are based on 993 samples of pigments from 70 Swedish churches.

jects have been analysed. Among them smalt was identified on many objects like altarpieces, epitaphs, pulpits etc.

In Norway, about 1 000 churches were built during the Middle Ages, most of them of wood. Today, only 31 wooden stave churches and 157 medieval stone churches remain. Besides, in comparison with Sweden and Denmark there are comparatively few murals in Norway (Andresen & Plather 1974), and quite few of them have been chemically analysed. On the other hand, there are many beautiful polychrome sculptures with original paint in the Norwegian churches, which have been examined and analysed. The following pigments have been found on these: carbon black, lime, chalk, cinnabar, ultramarine, gold, silver, tin foil, azurite, lead white, minium (red lead), lead tin yellow, verdigris (copper acetate), copper oleates, copper oxalate, and copper chloride (Andresen & Plather 1974; Plather 1995; 2002; Streeton 2013; 2016; Kollandsrud 2018; Kollandsrud & Plather 2019; Platania et al. 2020). Linseed oil or proteins were the most common binding media used. In comparison between Scandinavia and Great Britain, an overwhelmingly large number of pigment studies have been undertaken in the latter country (Howard 2003).

Discussion

What we can observe today on the walls and vaults in our medieval churches deviates from what could be observed on the fresh paintings during the Middle Ages. For instance, organic dyes are today almost invisible due to bleaching from sun and darkening from soot and other dirt, insects, bacteria etc. Many pigments have transformed into another chemical product. It is now well known that lead pigments like lead monoxide (PbO), minium (Pb₃O₄) or lead white may transform into black plattnerite (β-PbO₂). For the same reason, lead tin yellow may have turned grey (fig. 1).

For some reason, this oxidation of lead pigments is not observed on wood, so the acidity of the ground seems to have a protecting function. An example is given in fig. 2, showing a man wearing an orange dress painted with minium (red lead; Pb₃O₄). On the alkaline lime ground,

the minium has almost completely oxidized to black plattnerite. In contrast, this oxidation has not occurred on the slightly acidic oak log containing acids like gallic acid, salicylic acid and coumaric acid. In rare cases, though, we found that the expected oxidation of minium on lime had not taken place. Usually these murals had been treated with an organic substance such as a drying oil, which possibly has prevented the oxidation of lead. Another pigment, the blue azurite, may transform into black tenorite (CuO) or green malachite, but this was seldom observed in our studies. In coastal areas with salty winds, we found that azurite on a Gotland outdoor portal had reacted with salt (NaCl) from the Baltic Sea to form green atacamite, Cu₂Cl(OH)₃.

The green pigments malachite (a copper carbonate) and atacamite, [Cu₂Cl(OH)₃] will now be discussed. As mentioned above, malachite is very common in the Swedish murals, but uncommon in Danish murals where instead atacamite is usually found in green paint. This is curious, since malachite is a common mineral while atacamite is rare. The authors suggest that this difference may be caused during the process to transform lime (calcium carbonate) into calcium oxide (CaO), which is then slaked with water to give calcium hydroxide for the ground and the paint. It is likely that in Denmark salt Sea water was used for this slaking procedure, thus introducing salt (sodium chloride) into the ground and paint. This chlorine has later reacted with malachite in the paint to give atacamite, with almost the same colour. In Sweden, freshwater must have been used for the slaking, because we have only found chlorine once in a Swedish mural (excepting the chlorine in atacamite crystals). This only exception was observed on a 14th century mural in the Vadstena monastery, where (for some unknown reason) chlorine was identified.

Atacamite has been found in many medieval Swedish murals, although it is not quite as common as malachite. For some reason, atacamite was particularly common in the medieval murals in the Gotland churches. However, no chloride was found in these murals, so the atacamite is certainly not a transformation product of malachite and chlorine. The atacamite may



Fig. 1. St. Mary and Elizabeth in a painting by Albertus Pictor (Härnevi Church). The two haloes were originally painted with lead tin yellow. Photo: Maj Nord.



Fig. 2. “The man with the orange dress”. Mural in Härkeberga Church (Uppland) by Albertus Pictor (†1509). Photo: Kate Tronner.

have been imported from continental Europe or Russia, but it might also have been chemically prepared from copper sheets, salt (NaCl) and oxygen in the air. This method was early described by the 12th century writer Theophilus (Dodwell 1961), and it has been verified by the authors. It is symptomatic that atacamite is often found on bronze statues near the Sea (Nord et al. 2001). Accordingly, it cannot have been difficult to synthesize atacamite in the Middle Ages. For further information, compare a paper by Nord & Tronner (2018), in which also the four polymorphic forms of atacamite are presented.

The origin of the various pigments is certainly of interest. In medieval Scandinavia, common pigments like lime, carbon black and iron oxides/hydroxides were retrieved locally. For some other pigments, their origin can be determined from isotope measurements. For instance, lead oxide pigments were early prepared from molten lead produced from the mineral galena, PbS. Sixty lead-containing pigments from medieval Swedish paintings have been analysed by mass spectrometry for their lead isotope composition. By use of the OXALID data base (Stos-Gale & Gale 2009), we found that 90% of our lead pigment samples indicated a possible origin from four regions: Harz and Erzgebirge in Germany, the Pennines in Great Britain, or Sardinia in Italy, all these with a similar lead isotope composition (cf. Nord et al. 2015). Among them, the two German mining districts seem to be most likely. As regards the other six lead pigments, we found that they originated from Russia, the Swedish “Bergslagen” region in Västmanland, and from Värmland/Dalsland. Further elements have also been used to provenance pigments or artefacts from isotope measurements. For instance, Spangenberg et al. (2010) have analysed samples of cinnabar from ancient paintings; cf. also Nord and Billström (2018) for further examples.

Another method to settle the origin of a pigment is based on the presence of secondary minerals. For instance, Aru et al. (2014) have analysed azurite minerals from various European sources and were able to provenance samples of this blue pigment from the presence of small amounts of secondary minerals. The present au-

thors have in nine Swedish churches identified *volborthite*, a rare yellow copper vanadate mineral with the chemical formula $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. These volborthite grains were always found in malachite-painted murals, within a limited period of time (1430–1490) and within a limited geographic area (Uppland and Södermanland). By use of published data for malachite deposits in northern Europe exploited during the second half of the 15th century, we could conclude a German origin (Nord et al. 2012). Naturally, the study of trace elements may be a third method for provenancing mineral pigments and other objects.

During the first two centuries of the Middle Ages, the Scandinavian countries invited foreign painters from Germany, England or Russia to decorate their new churches. When the building of the large Danish cathedrals in Roskilde and Lund was finished, many foreign craftsmen had to search for work elsewhere, some of them on Gotland. On this large island there still remain murals and wooden panels (from demolished stave churches) with a Byzantine painting style, most likely performed by Russian painters (fig. 3) (Nord et al. 2017). With time, domestic painters came to replace most of the foreign labour. Hundreds of painters must have been at work during the later Middle Ages. Unfortunately, surprisingly few of these early painters are known by their names. The most renowned painter working in medieval Sweden was Albertus Pictor (†1509), who emigrated from Germany around 1460. Another painter active during the 15th century is the “Passion master”, who has decorated about thirty medieval Gotland churches, all with a typical style and a very limited palette (fig. 4). But his nationality is still unknown.

In rare cases, the analysed pigments can help to date a painting. For instance, lead tin yellow was introduced during the 14th century, and ultramarine and lead white are rare in Sweden after the 13th century. Smalt was introduced later. As regards help with attribution, two examples have been given in an earlier paper discussing Albertus Pictor’s paintings (Nord et al. 2018). There was a question whether the paintings in Nederluleå Church (north Sweden) and those in the chapel of Öja Church (Gotland) might have



Fig. 3. Byzantine paintings from the 12th century. Painted boards preserved from a since long demolished stave church at Dalhem, Gotland. Photo: A. G. Nord.



Fig. 4. Painting from the 15th century by the “Passion Master” in Ganthem Church, Gotland.
Photo: A. G. Nord.

been painted by Albertus Pictor. In this case, the pigments in Nederluleå Church agreed well with Albertus Pictor’s traditional palette, while they disagreed for the Öja paintings.

It is also interesting that many of the medieval pigments listed in Table 1 were also imported and used by the Vikings. Traces of pigments from Swedish runic stones have been analysed (Tronner et al. 2002). The following pigments were found: carbon black, lime, iron oxides, cinnabar, azurite, ochre, umber, minium (red lead; Pb_3O_4), lead monoxide (PbO) and lead white [$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$]. Also in Denmark, some painted wood objects from the Viking Age have been analysed (Christensen 2018). The following mineral pigments were identified: carbon black, lime, chalk, iron oxides and iron hydroxides, cinnabar, vivianite, yellow and red ochre, orpiment, malachite, atacamite, umber and various lead

oxides. Paint has also been found on Norwegian Viking Age objects, with pigments similar to those found in Denmark and Sweden.

Conclusions

Based on the results presented in the previous section, the authors conclude that, with some exceptions, about the same pigments were used during the Viking Age and during the Middle Ages for most Scandinavian paintings. Ordinary pigments like carbon black, lime, iron oxide/hydroxide and red ochre were retrieved locally in the three countries. Many of the other pigments were probably imported from Germany, in particular those containing copper or lead, but probably also smalt and some earth pigments. For green, malachite was often used in the murals. In the Danish murals, the malachite has with time been transformed into atacamite,

possibly due to chloride in the slaked lime. Verdigris (a green copper acetate) was used to paint wooden sculptures. For some reason, smalt seems to be rare in Swedish medieval paintings in comparison with Denmark and Norway. The lead-containing pigments as well as smalt are synthetic products. More uncommon mineral pigments like ultramarine, cinnabar, orpiment, and gold must have been obtained from merchants within the Hanseatic League. The Scandinavian countries early became members of the Hanseatic League (around 1150–1600 AD), and were represented by Scandinavian towns like Copenhagen, Roskilde, Bergen, Stockholm, Kalmar and Visby. There was also an important trading exchange between Sweden and Russia. Many Russian tradesmen lived in the town Visby on Gotland, and many Swedish tradesmen were busy in Novgorod, situated about 100 km south-east of present St. Petersburg. The pigments used for the Swedish murals differ slightly from what was commonly used on the European continent and in Great Britain. It is noteworthy that smalt and Naples yellow are not included in the excellent compilation by Howard (2003). Vivianite and atacamite seems to have been more common in Sweden, while orpiment was less common.

Another conclusion is that chemical analyses of a painting may provide useful information for conservators and art historians. Pigments and binding media can be determined, and observed colour changes may be explained. The presence of modern pigments like barium sulphate and chromium oxide in a medieval painting reveals that measures not allowed today have earlier been undertaken. Isotope data or secondary minerals in a pigment may help to settle the origin of that pigment. It may finally be added that for oil paintings produced after the 15th century, isotope data for lead white and other lead pigments have been used to settle doubts on genuineness of works by old masters (Fleming 1975; Fortunato et al. 2005).

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