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Original article

Lead isotope data for provenancing mediaeval pigments in Swedish mural paintings

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ABSTRACT

A plausible origin of lead can often be proposed from its stable isotope ratios. The isotopic composition of 28 lead pigments from mediaeval mural paintings in 14 churches in south Sweden were analyzed. In general minium (Pb_3O_4) or its oxidized transformation product plattnerite (β-PbO_2) was analyzed. A number of churches share similar Pb isotope signatures, and tentatively it is possible to distinguish a number of different isotope signatures suggesting various origins of lead. Although lead ore was mined in the Bergslagen ore district (south-central Sweden) during Mediaeval times, there is no isotopic match between Bergslagen ore data and any of the pigments. Based on the lead isotope data and other lines of evidence, we presume that the majority of lead pigments most likely originate from Harz (in the center of Germany) and Erzgebirge (between Sachsen and Bohemia). The results also indicate that usually the different lead pigments taken from an individual church have the same isotopic composition, i.e. indicating the same origin. An exception is the Mästerby church (Gotland), with paintings in a Russian-Byzantine style. Its lead isotope signatures are heterogeneous, and for some material a Russian origin is instead suggested.

1. Research aim

This methodological study is a contribution to ascertain the provenance of mediaeval pigments from Swedish mural paintings. Earth colours, soot and lime were easily obtained locally in Europe, while mineral pigments like malachite or cinnabar usually were imported from neighbouring or more distant countries. Stable isotopes may be used to determine the provenance of lead pigments or cinnabar (HgS). The paper describes an investigation involving lead pigment samples from mediaeval church murals in the south of Sweden. As shown from this study, lead isotope compositions in combination with other observations can often help pinpointing a possible origin of the lead.

2. Introduction

Hundreds of mediaeval churches in Sweden possess more or less well-preserved murals painted *al secco* on lime grounds. The authors have documented and analyzed some of their pigments [1–3]. In these studies 23 different pigments were identified (disregarding modern pigments used for later "improvements"). From time to time, questions on their provenance have been raised. Earth colours, soot and lime/chalk were found locally, while mineral pigments which are not found in the Swedish bedrock must have been imported. Foreign painters may have brought their own painting material with them, or the material may have been acquired in Sweden from foreign tradesmen.

In a previous study, the origin of malachite pigments in five mediaeval churches in Sweden could be settled owing to small impurities of a rare yellow vanadate mineral, volborthite, with the chemical composition $Cu_3(V_2O_7)(OH)_2{\cdot}2H_2O$ [4]. Very few mediaeval European ore deposits contained both malachite and volborthite, five of them in Germany. The presence of this unusual mineral combination was taken to indicate an origin from Harz or Schwarzwald. Inspired by the above-mentioned study, which included three churches also forming part of the present study (Table 1), we have now analyzed 28 lead-containing pigments from mediaeval murals with respect to their Pb isotope ratios. The ultimate aim is to constrain the provenance for these pigments. So far quite few isotope studies of older pigments have been undertaken [5,6].

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Table 1
The churches, painter (if known) and dating, and number of lead samples used to determine the relative natural isotope abundance.

Region	Church	Painter	Dating	Number of lead pigments analyzed with a mass spectrometer
The Mälaren valley	Härkeberga[a]	Albertus Pictor. Paintings after *Biblia Pauperum*	Around 1490	4
	Täby[a]	Albertus Pictor. Paintings after *Biblia Pauperum*	Around 1490	1
	Risinge old church[a], 100 km SW of the Mälaren valley	The "Master of Risinge"	Around 1430	1
Gotland	Anga	"The Passion Master"	Mid 1400s	1
	Bro	"The Passion Master"	Mid 1400s	1
	Bunge	Anonymous. Influence from Bohemian art	End of 1300s	2
	Garde	Russian-Byzantine painting	Around 1150	1
	Lye	"Egypticus"	Around 1350	2
	Martebo	Anonymous. German influence	Mid 1300s	2
	Mästerby	Russian-Byzantine painting	Around 1200	4
Scania	Brönnestad	Anonymous	Around 1400	2
	Fjelie	Late Roman paintings	Around 1150	3
	Malmö, St Petri Cathedral	Anonymous. German influence	Ca. 1520	1
	St. Köpinge	The "Master of Snårestad"	Around 1300	3

[a] Provenancing of malachite pigment in this church has been made [4].

During the Middle Ages hundreds of ore deposits were worked in Europe and elsewhere. The largest mining district in Europe was the Erzgebirge, between Sachsen and Bohemia. Mediaeval lead mining has also been documented from several other places in Germany and in countries such as present Czech Republic, England, Poland, Sweden, Austria, France and Italy (Fig. 1). The most common ore mineral for production of metallic lead is galena (PbS), but also cerussite ($PbCO_3$) and massicot (PbO) were used. The Romans made lead white ($2PbCO_3{\cdot}Pb(OH)_2$) by reacting metallic lead with acetic acid. (This substance also exists as a rare mineral, hydrocerussite). The mineral massicot was used as a yellow pigment. Red minium (Pb_3O_4) was made by heating lead white or massicot. Lead tin yellow ($\sim PbSn_2SiO_7$) was manufactured much later, at the end of the Middle Ages, probably in glass works. It is now well known that many lead pigments in murals may be oxidized to black or dark brown plattnerite, the tetragonal modification of lead dioxide (often denoted β-PbO_2) [1,7].

Lead exists with four stable isotopes having mass numbers 204, 206, 207 and 208. With the exception of ^{204}Pb, they have been (and still are) formed from radiogenic decay of uranium or thorium. Since this decay is extremely slow, the geological age of the mineral deposit is an important factor for its lead isotopic composition. For Pb-rich ores, in which Pb has been separated from U and Th by geological processes, no significant *in situ* decay of U and Th takes place after their formation, thus implying that their Pb isotope ratios carry a "fossil record" that represents their time of formation. This is the reason why the isotopic variations in the lithosphere may be considerable, which is favourable when attempting to use Pb isotopes to reveal the provenance of the lead in e.g. an artefact. The relative isotopic abundance is usually given by the three ratios $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, using ^{204}Pb as a reference isotope [8]. In archeological research it is customary to display data in $^{206}Pb/^{204}Pb$ *versus* $^{207}Pb/^{206}Pb$ or $^{208}Pb/^{206}Pb$ diagrams, respectively, and numerous reference data from ancient mining districts are reported in this way. The isotopic composition of a lead-bearing substance is identical to that of the lead ore from which it was once manufactured, and this fact forms the basis for using measured Pb isotope compositions of lead-bearing artefacts or pigments as a fingerprint of the origin of the lead. A disagreement between data for sample and ore deposit, respectively, *definitely* shows that the analyzed lead cannot originate from the deposit in question. An agreement ("match") indicates that the lead *may* originate from that specific deposit. It must also be remembered, with the accuracy of the data taken into account that an overlap of isotopic fingerprints may exist between different ore districts. Moreover, a painter may have mixed pigments from different sources, and (for natural reasons) lead isotope data are not available for all possible ore districts. Accordingly, a definite answer as to the provenance of a lead-bearing object ore district may seldom be achieved. However, independent evidence may help to pinpoint the most likely provenance, as shown in the text below.

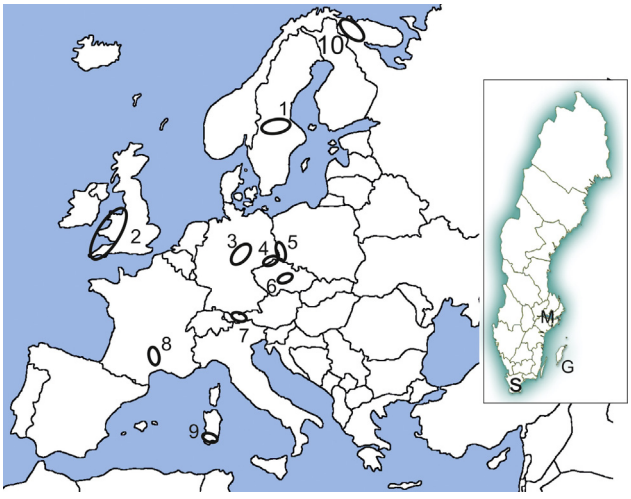

Fig. 1. Map of Europe showing some important historical ore mining districts. Abbreviations: 1 = Bergslagen district, Sweden; 2 = Wales-Cornwall, UK; 3 = Harz, Germany; 4 = Erzgebirge, near the German-Czech border; 5 = Silesian district, Poland; 6 = Kutná-Hora, Czech republic, 7 = Tyrol area, Austria; 8 = Ardennes area, France; 9 = Iglesiente-Sulcis area, Sardinia; 10 = Kola peninsula, Russia. The inset map shows the studied regions in Sweden: S = Scania (Skåne), G = Gotland and M = Mälaren Valley.

3. Experimental

The study has been concentrated to church murals in three regions in south Sweden:

- Scania (*Skåne*) near the European continent;
- the Mälaren Valley west of Stockholm;
- the island of Gotland in the Baltic Sea, during the Middle Ages a prosperous commercial center (Fig. 1).