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Lead isotope heterogeneity in lead white: From lead white raw pigment to canvas

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ABSTRACT

The heterogeneity of lead isotope ratios of lead white paints within individual paintings is evaluated. The analyses of five different 17th-century Dutch paintings, sampled in different locations, identifies the presence of isotopic heterogeneity in lead white within a single painting. Pure pigment in the form of cones of 16th-century Venetian lead white, in contrast, was found to be isotopically homogeneous. The study evaluates the origins of the increased heterogeneity of lead isotope ratios in the evolution from the pure pigment to the artwork.

1. Introduction

Lead isotope analysis has been widely used in archaeology and cultural heritage for the provenance of artefacts [1,2] and successfully applied to paintings to distinguish different sources of lead in lead white pigments [3–7]. It has also proved possible to use lead isotope ratios to distinguish artistic groups, for example Italian 16th-century and Netherlandish 17th-century artists [5]. Lead isotope analysis on paintings, however, has always been limited by the amount of material and number of samples available, due to the imperative to avoid destructive analysis. The limited sample availability translates to a lack of knowledge on the variation of lead isotope ratios within and between paintings. Currently there is little understanding of the level of isotopic variation within an individual artist's oeuvre, an historical period or geographical region. More importantly there is a lack of knowledge of lead isotope variation within a single painting. Therefore, the information that can be extrapolated from an individual lead isotope analyses of a painting is limited and the interpretation of the results is based on poor constraints in relation to the temporal and spatial variations in lead based paints. Incomplete understanding of the isotopic variations in paintings makes analyses of the isotopic data open to interpretation, particularly when questions of authentication are involved. The *Saint Praxedis* (1655, Private Collection) tentatively attributed to Vermeer, is

a good example [8]. One argument for the attribution to Vermeer is based on comparison of the Pb isotope analysis of two lead white samples from the *Saint Praxedis* and a lead white sample from Vermeer's *Diana and her Nymphs* (1653-4, Mauritshuis, The Hague, inv. 406). The Pb isotope analyses of the two paintings are statistically identical and this evidence was used to support an attribution to Vermeer (Christie's London Auction Cat. July 2014, The Barbara Piasecka Johnson Collection, Lot 39.). The interpretation was based on the assumption that samples from works by the same artist have the same isotopic ratios. Based on the current state of knowledge, however, this assumption is not proven. On the contrary, the literature data show that the Pb isotope ratios of lead white can vary within the oeuvre of an individual artist [4]. Using these considerations as a starting point, this paper aims to:

- Characterise the level of lead isotope heterogeneity of lead white within a single painting, studying five individual paintings by four different Netherlandish artists from the 17th century. Samples from different areas and layers in the paint build-up of the paintings are compared to characterise the level of isotopic heterogeneity.
- Characterise the level of heterogeneity of lead isotope ratios within seven cones of pure 16th-century Venetian lead white pigment that were recovered in a shipwreck off the coast of Croatia. The results will be used to constrain the lead isotope variation in commercially

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manufactured lead white pigments and hence the variation expected within individual paintings.

- Investigate the implications of any lead isotope heterogeneity in lead white for future data interpretation.
- Use observations of the extent of lead isotope heterogeneity to advise on the basis for the creation of a comprehensive database containing information of lead isotope ratios of lead white.

These data will represent the start of a database that will cover 17th-century Dutch paintings. The aim of the database is to provide art historians and conservators with more reliable information to aid in identification, authentication and provenancing of unknown paintings, while at the same time providing an indication of how the trade in lead was influenced by social-economic factors.

1.1. Lead white

Lead white was the most important white pigment used in easel painting until the nineteenth century [9], therefore the study of the lead isotopes of this pigment can provide information about trading practices on a long socio-historical timescale. Lead-white is composed predominantly of lead carbonate that occurs in two main crystalline forms; cerussite (PbCO_3) and hydro-cerussite ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) [10]. The main methods of lead white synthesis consist of exposing metallic lead to acetic acid, either by submerging it in vinegar, or by the so-called 'Dutch stack process'. In the latter, strips of lead were placed over vinegar in earthenware pots and surrounded by dung to provide heat and carbon dioxide that would speed up the reaction. After several weeks the lead surface would have reacted to form a lead carbonate. This carbonate would be scraped off, washed and dried [9]. The pigment then receives post-synthesis treatments such as washing, grinding of the pigment in water or in acidic solutions (vinegar), heating in water and levigation. These processes allow selection of pigment particles by size [11]. Historical sources reveal that different qualities of lead white were produced, some of which were mixed with chalk and hence less pure, and sold at different prices. Workshop practice at the time was 'clean', aimed at keeping the different pigments separate during preparation, such as grinding and mixing with a binding medium, and storing until use [10]. The lead white would then be mixed with other pigments on the palette and pre-processed oil (e.g., where litharge is added or treated in order to speed up the drying process), just before application [12–14]. The availability and usage of different quality lead white pigments raises the question whether one or more sources of Pb ore were used in manufacturing lead white pigments.

1.2. Known variability of lead isotopes

1.2.1. Variability of lead isotopes in lead deposits

Lead isotope heterogeneity is a documented phenomenon that occurs at different levels. There is major variation in lead isotope ratios within and between lead ore deposits that can be exploited to infer the origin of lead minerals used to produce lead white (OXALID (<https://oxalid.arch.ox.ac.uk/>), [1]). The high variation of Pb isotope ratios in ore deposits is caused by variability in both the nature of the geological process that leads to the formation of lead deposits, and the absolute time of formation. Lead has four stable isotopes ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb . ^{204}Pb is non radiogenic while ^{206}Pb , ^{207}Pb and ^{208}Pb are the product of radioactive decay of respectively ^{238}U , ^{235}U and ^{232}Th . The Pb isotope ratios in Pb-rich minerals formed in mineral deposits vary dependent on the source of the mineralising magmatism and ore fluids, which in turn are controlled by the specific geological settings and time [15,16]. Lead ore deposits were formed at markedly different times, from the Archaean (>2500 million years) to the present day [16]. This has resulted in a marked variation in Pb isotope ratios in ore minerals, both locally and regionally, which reflects the time-integrated levels of U, Th and Pb in the geological setting [15,17]. For example, the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio in lead

ore deposits ranges from <15.0 to >22.5 [16]. The lead present in these deposits, when extracted, retains the isotopic composition of the original ore minerals. Assuming that significant mixing of lead from different mines is avoided, this composition will be transferred to the materials and artefacts containing the lead. The level of Pb isotope heterogeneity inherited by lead white pigment during the production process is, however, unknown. This assessment is fundamental to understand how to interpret lead isotope data.

1.2.2. Variability of lead isotopes in paintings

Lead isotope variation of the ores is recorded directly in the lead isotopes of lead white. This variability has for example been observed in lead white used by 17th-century Netherlandish artists and 16th-century Italian painters [4,5]. Lead isotope ratios, in this case, show that Italian and Dutch paintings are easily distinguishable and cluster in two groups. Data from Netherlandish paintings indicate that Pb isotope ratios vary between 18.41 and 18.48 and 15.61–15.64 in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, respectively [5]. This variation corresponds to circa 22 and 10 times the analytical resolution of a modern multi-collector mass spectrometers, and is representative of the heterogeneity of lead isotope ratios present in 17th-century Dutch/Flemish paintings. The lead isotope distribution in this group indicates that, without additional information, it is impossible to clearly distinguish different artists, or paintings, using only lead isotope ratios. Moreover, the lead isotope ratio variability within a painting has not been systematically studied, leaving a gap in the information obtainable from lead isotopes. This variation in particular could have a crucial role in data interpretation.

1.2.3. Variability of lead isotopes in individual paintings

A pilot study was performed on Vermeer's *Girl with the pearl earring* (c.1665, Mauritshuis, The Hague), to assess the question of lead isotope ratio variability in an individual painting. Lead isotope analysis was conducted on different paint layers, containing different lead whites with different cerussite/hydro-cerussite ratios. While the different layers did not show a correlation between lead isotope ratios and cerussite/hydro-cerussite ratios, the pigments of two samples recorded an isotopic variation outside analytical error (van Loon et al. 2019, samples 7 and 16a [7]). The paper concludes that: "there are several plausible explanations for the small degree of heterogeneity of the lead isotopes of the ground layer. First, the lead white is present in a mixture with other pigments. Moreover, the lead ore deposits are not fully homogeneous due to the fact that the geological processes that form the lead ore operate on a scale of >10 km and result in ore fluids interacting with different types of rocks beneath where the ore is ultimately formed. Additionally, lead white pigment production could potentially include a minor component of recycled lead. It is also possible that minor amounts of Pb-containing dust and other contaminants (<0.01%) were introduced during pigment production, paint making or paint application. All these processes potentially lead to detectable isotopic variations, which does not obscure the ultimate source of the Pb" [7]. These observations are the base for this investigation of the heterogeneity of lead isotopes in lead white in individual paintings.

2. Paint samples

Five 17th-century Dutch paintings by four different painters from the Rijksmuseum were analysed.

- Gerard van Honthorst. i) *Portrait of Willem II (1626–1650), Prince of Orange, and his Wife Mary Stuart (1631–1660)*, 1647, Rijksmuseum, SK-A-871, oil on canvas, w 194.4 cm × h 302 cm. (<https://www.rijksmuseum.nl/en/collection/SK-A-871>)
- ii) *Portrait of Friedrich Wilhelm, Elector of Brandenburg, and his Wife Louise Henriette, Countess of Orange-Nassau*, 1647, Rijksmuseum, SK-A-873, oil on canvas, w 194.4 cm × h 302 cm. (<https://www.rijksmuseum.nl/en/collection/SK-A-873>)

These two paintings, together with *Frederick Henry, his Consort Amalia of Solms, and their three youngest daughters* (SK-A-874), form an ensemble made for Huis den Bosch in 1647. Due to similarity in theme, size, and identical year of production, the paintings SK-A-871 and SK-A-873 are likely to be painted in Honthorst's studio at the same time using materials presumably purchased specifically for this commission.

- Aert de Gelder, *Hermanus Boerhaave (1668–1738), Professor of Medicine at the University of Leiden, with his Wife Maria Drolenvaux (1686–1746) and their Daughter Johanna Maria (1712–91)*. 1720 – 1725, Rijksmuseum, SK-A-4034, oil on canvas, w 173 cm × h 104.5 cm. (<https://www.rijksmuseum.nl/en/collection/SK-A-4034>)
- Jacob de Gheyn (II), *A Spanish stallion Captured by Lodewijk Gunther van Nassau from Archduke Albert of Austria in the Battle of Nieuwpoort and Presented to Prince Maurits*, 1603, Rijksmuseum, SK-A-4255, oil on canvas, w 269 cm × h 228 cm. (<https://www.rijksmuseum.nl/en/collection/SK-A-4255>)
- Jan van Goyen, *View of a Town on a River*, 1645, Rijksmuseum, SK-A-120, oil on canvas, w 165.5 cm × h 131 cm. (<https://www.rijksmuseum.nl/en/collection/SK-A-120>)

More specific information about the paintings can be found on the Rijksmuseum website (<https://www.rijksmuseum.nl/en/search>) using the Rijksmuseum inventory numbers listed above and in Table 1.

The second batch of samples were obtained from pure lead white pigment transported as cones, with an average weight of 420 g, Fig. 1. These cones were recovered from the ship *Gagliana Grossa*, sunk in late October or early November of 1583, near the island of Gnalčić, off the central coast of the eastern Adriatic, present-day Croatia [18]. Archival research revealed the merchant ship was on route from Venice, loaded with cargo intended for the markets of Constantinople [18,19]. The cargo consisted of various products of European manufacture, including a large quantity of colouring materials packed in casks or barrels, stowed in the ship's hold [20]. The largest volume of colouring materials preserved on the shipwreck was lead white, loaded in casks with a monogram composed of a cross and the letters S and Z. Today, after submersion in seawater, the surface layer of the cones is composed of black and/or dark grey galena (lead sulphide), formed through reaction with sulphur-based components in the shipwreck cargo and seawater [20]. The lead white cones preserved in their raw form provide a unique opportunity to examine the lead isotope heterogeneity in a mass produced 16th century-pigment before its use.

3. Sampling and analytical method

The sampling procedures used to obtain lead white are described below and the number of the samples and mode of sampling summarized in Table 1.

- The two Gerard van Honthorst paintings and the Jan van Goyen were sampled directly by a trained conservators who manually removed a microscopic amount of paint from areas rich in lead white using a surgical scalpel. In order to have a good spatial sample coverage, when possible the paintings were sampled in 5 different areas. The samples were collected by carefully placing the scraped material into pre-cleaned (2 M HNO₃) centrifuge tubes.

- The Aert de Gelder painting was sampled following the same procedure with one exception. For this painting 10 samples were collected, divided in two groups. Five samples were taken from original lead white paint and 5 samples were gathered from documented 19th-century retouchings of the painting. In this way it was possible to study the heterogeneity of two generations of lead white and evaluate the ability of lead isotope analysis to discriminate between them.
- The very large and damaged Jacob de Gheyn (II) was undergoing extensive restoration at the time of sampling and two sampling procedures were used. Nine scraped samples were collected manually by conservators as described above. The second set of lead white pigment samples were obtained from cross sections using a micro scalpel in a procedure described elsewhere in detail [21]. The micro scalpel allows the operator to sample particles of lead white directly from a single paint layer in a microscope cross section. Typically, a sample furrow measures 10–50 µm in width. The micro scalpel allows the possibility to study the mineralogical and lead isotope ratio distribution between different pictorial layers of a painting. For the De Gheyn painting, 6 paint cross sections were available and 12 samples were collected. In total, 21 samples were obtained from the painting to study the 3 dimensional distribution of Pb isotope ratios.
- Seven of the several hundred recovered Venetian cones were chosen to study the variation of lead isotope ratios in the commercially manufactured pure lead white pigment. The cones were cut in half using a hand-saw. This revealed a black lead-sulphide layer, 1–5 mm thick that covers the cones (Fig. 1b). The interior of the cones, however, away from cracks, was found to be unaffected by the blackening process. For each cone, 4 and 5 samples were collected from the white part using a plastic pin. A total of 30 samples were collected as powder and transported in pre-cleaned (2 M HNO₃) centrifuge tubes.

The samples were prepared for isotopic analyses following the method described in detail in D'Imporzano et al. 2020 [21]. In brief, samples were dissolved in 1 mL 2 M HNO₃ and solutions transferred to 7 mL Teflon beakers, dried down and re-dissolved in 0.2 mL 0.7 M HBr. The solution was then processed by liquid chromatography using AG®1-X8 anion exchange resin (analytical grade, 200–400 mesh, chloride form) to separate the Pb fraction from the samples matrix. The concentration of the Pb fraction was determined by inductively coupled plasma mass spectrometry (ICPMS). Once Pb concentrations were known, 2 mL 1% HNO₃ solutions were made containing 100 ng of Pb (50 ppb). The solutions were analysed using a Thermo Scientific Neptune multi-collector-ICPMS using standard sample bracketing (SSB) to correct for instrumental mass fractionation. For each batch of 18 analyses, a NIST NBS981 lead solution, two in house internal standard solutions (pure lead solution prepared from a CPI International solution) and a total procedure blank were analysed to monitor data quality. The blank solutions, prepared following the same procedure as the samples, monitor the amount of external lead introduced during the sampling and the sample preparation. The analyses of the blank solutions was performed by isotope dilution with a ²⁰⁸Pb spike solution of known concentration and isotopic composition.

Measurements were performed using a desolvating nebulizer system, CETAC Aridus II, operating at approximately 4–5 L min⁻¹ of Ar sweep

Table 1

Name of the Artist, material sampled, sampling technique, type of sample obtained and number of samples obtained.

	Object	Sampling method	Sample type	N. of samples	Birth-Death (active)
Gerard van Honthorst's	paintng	manual	scraping	10	1592–1656 (1610–1656)
Jan van Goyen'	paintng	manual	scraping	5	1596–1656 (1620–1656)
Aert de Gelder's	paintng	manual	scraping	10	1645–1727 (1660–1727)
Jacob de Gheyn II	paintng	manual and microscalpel	scraping	21	1565–1629 (1585–1629)
Venetian cones	raw pigment	manual	powder	30	Before 1583



Fig. 1. Left, exterior view of a Venetian lead white cone and right interior view of a cone that was cut in half. Note galena-rich rim. Yellow dots mark sampling locations. Approximate cones size: width, 5 cm at the bottom 8 cm at the top; height 7–10 cm; weight circa 500 gram.

gas, $0.01\text{--}0.02\text{ L min}^{-1}$ nitrogen and with temperature settings of $110\text{ }^{\circ}\text{C}$ for the spray chamber and $160\text{ }^{\circ}\text{C}$ for the membrane. Lead ion beams were about 0.2 V ppm^{-1} and were measured on Faraday cups equipped with $10^{11}\ \Omega$ amplifiers. A gain calibration was performed on the $10^{11}\ \Omega$ amplifiers once per week. An analysis consisted of one block of 100 cycles of 4 s integration time. The instrument operated with a RF power of 1290 W. Faraday cup detectors were assigned to the following masses: ^{201}Hg L4, ^{202}Hg L3, ^{204}Pb L2, ^{205}Tl L1, ^{206}Pb C, ^{207}Pb H1, ^{208}Pb H2, ^{209}Bi H3. The long-term precision, expressed as 2 standard deviations (SD) of analyses of the NIST NBS981 over two years ($n > 100$), was 0.0031 for $^{206}\text{Pb}/^{204}\text{Pb}$, 0.0034 for $^{207}\text{Pb}/^{204}\text{Pb}$, 0.0114 for $^{208}\text{Pb}/^{204}\text{Pb}$, 0.00009 for $^{207}\text{Pb}/^{206}\text{Pb}$ and 0.00033 for $^{208}\text{Pb}/^{206}\text{Pb}$.

4. Results

The values obtained for all the NBS981 standard solutions analysed for this study were within analytical uncertainty of literature values (e. g., Thirwall, 2002 [22]). Total procedure Pb blanks varied between 5 and 60 pg indicating that the blank contribution to the isotopic composition of the samples is negligible. The Pb isotope data for the lead white samples are presented in Table 2 and Figs. 2–4. Every figure includes the long term precision of the instrument as a cross on the top left part of each graph.

For both Gerard van Honthorst paintings, SK-A-871 & 3, Pb isotope ratios range from 18.475 to 18.488 for $^{206}\text{Pb}/^{204}\text{Pb}$, from 15.631 to 15.645 for $^{207}\text{Pb}/^{204}\text{Pb}$ and from 38.441 to 38.475 for $^{208}\text{Pb}/^{204}\text{Pb}$ (Table 2, Fig. 2a and b). For the SK-A-873 painting, lead isotopes vary from 18.468 to 18.488 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.627 to 15.645 for $^{207}\text{Pb}/^{204}\text{Pb}$ and from 38.435 to 38.492 for $^{208}\text{Pb}/^{204}\text{Pb}$. The average value for lead white lead isotopes of the two paintings is 18.479 ± 0.012 (2SD) for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.637 ± 0.011 (2SD) for $^{207}\text{Pb}/^{204}\text{Pb}$ and 38.455 ± 0.035 (2SD) for $^{208}\text{Pb}/^{204}\text{Pb}$.

Lead isotope ratios for lead white from the Jan van Goyen painting (Table 2, Fig. 2c and d) vary between 18.4745 and 18.480 for the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio and between 15.6401 and 15.644 for the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio and from 38.446 to 38.461 for $^{208}\text{Pb}/^{204}\text{Pb}$. The average $^{206}\text{Pb}/^{204}\text{Pb}$ ratio is 18.477 ± 0.004 (2SD), $^{207}\text{Pb}/^{204}\text{Pb}$ is 15.641 ± 0.004 (2SD) and 38.452 ± 0.013 (2SD) for $^{208}\text{Pb}/^{204}\text{Pb}$.

The lead white from the Jacob de Gheyn (II) painting (Table 2, Fig. 2e and f) has lead isotope ratios that vary between 18.416 and 18.439 for $^{206}\text{Pb}/^{204}\text{Pb}$ and between 15.625 and 15.634 for $^{207}\text{Pb}/^{204}\text{Pb}$ and from 38.392 to 38.430 for $^{208}\text{Pb}/^{204}\text{Pb}$. The average value for $^{206}\text{Pb}/^{204}\text{Pb}$ is 18.433 ± 0.011 (2SD), 15.630 ± 0.005 (2SD) for $^{207}\text{Pb}/^{204}\text{Pb}$ and 38.412 ± 0.022 (2SD) for $^{208}\text{Pb}/^{204}\text{Pb}$.

The results for the lead white cones are shown in Table 3, Fig. 2g and h. Isotope ratios from the 30 analyses from 7 different cones range from 18.376 to 18.382 for $^{206}\text{Pb}/^{204}\text{Pb}$, between 15.673 and 15.678 for $^{207}\text{Pb}/^{204}\text{Pb}$ and from 38.526 to 38.546 for $^{208}\text{Pb}/^{204}\text{Pb}$. The cones have an average of 18.379 ± 0.003 (2SD) for $^{206}\text{Pb}/^{204}\text{Pb}$ and 15.675 ± 0.003 (2SD) for $^{207}\text{Pb}/^{204}\text{Pb}$ and 38.537 ± 0.011 (2SD) for $^{208}\text{Pb}/^{204}\text{Pb}$.

Two different lead-white pigments were sampled from the Aert de Gelder painting, from retouching and the original paint. The results are presented in Table 2 and Fig. 3a and b and show a clear distinction between the two generations of paint. The retouching show greater heterogeneity compared to the original paint. The $^{206}\text{Pb}/^{204}\text{Pb}$ ratio vary from 18.229 to 18.275 while the variation for the $^{207}\text{Pb}/^{204}\text{Pb}$ is from 15.622 to 15.627 and from 38.196 to 38.247 for $^{208}\text{Pb}/^{204}\text{Pb}$. The average value for the retouching is 18.252 ± 0.041 (2SD) for $^{206}\text{Pb}/^{204}\text{Pb}$, for the $^{207}\text{Pb}/^{204}\text{Pb}$ is 15.623 ± 0.005 (2SD) and 38.220 ± 0.051 (2SD) for $^{208}\text{Pb}/^{204}\text{Pb}$. The original lead white, Fig. 3c and d, has Pb isotope ratios ranging from 18.443 to 18.463 for the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio, 15.630 and 15.635 for $^{207}\text{Pb}/^{204}\text{Pb}$ and from 38.436 to 38.459 for $^{208}\text{Pb}/^{204}\text{Pb}$. The average value for the original lead white $^{206}\text{Pb}/^{204}\text{Pb}$ is 18.449 ± 0.016 (2SD), while the average $^{207}\text{Pb}/^{204}\text{Pb}$ ratio is 15.631 ± 0.004 (2SD) and 38.449 ± 0.017 (2SD) for $^{208}\text{Pb}/^{204}\text{Pb}$.

5. Discussion

The Pb isotope data demonstrate that the extent of heterogeneity in lead white pigments differs from painting to painting. In order to fully understand the implications of these differences, two factors must be taken into account. First, despite the high precision of the individual analyses, two samples are only considered statistically different when their isotopic values differ by more than twice the 2 standard deviation (2SD) of the method. This quantity is determined by analysing an international Pb standard solution, NBS 981, multiple times over an extended interval of time (>1 year) [21]. Throughout the discussion, the 2SD will be used as a basic unit to discuss samples differences. To make the concept clear: the 2SD on the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio is 0.0031. Hence, if the value of sample X is 18.0000 and sample Y is 18.0075, the two differ by 0.0075, equal to 2.4 2SD, which means that X and Y are statistically different.

Secondly, mass dependent fractionation during analysis needs to be considered. This phenomena causes Pb isotope ratios to define slopes related the mass difference between isotopes in so-called 3-isotope-plots, e.g., a slope of ~ 1.5 in a $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot. This problem is extensively discussed in the literature and was only more easily overcome after the introduction of modern multi-collector mass

Table 2

Sample identification (Rijkmuseum ID), isotopic values for each sample with two times the standard error, 2SE, and sampling method. For the painting from Aert de Gelder the samples taken from the retouched parts are listed under the caption Retouching. Similarly for Jacob de Gheyn (II) the samples taken using the micro-scalpel are listed below the caption micro-scalpel.

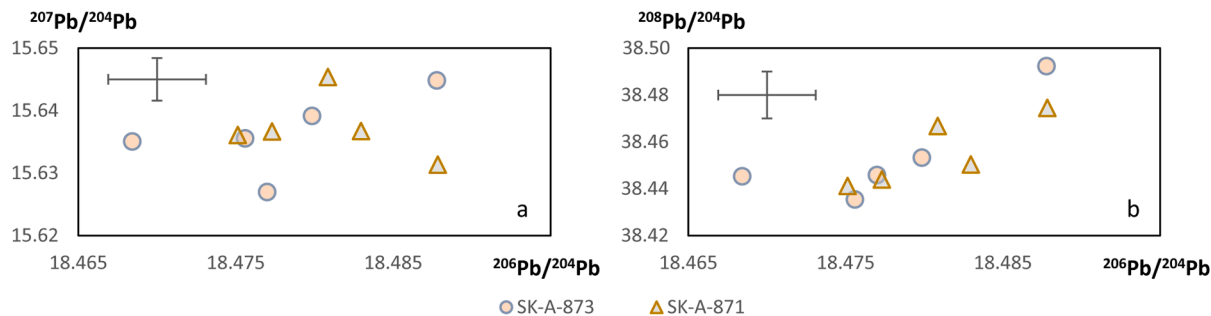
Rijkmuseum ID	$^{206}\text{Pb}/^{204}\text{Pb}$	2SE	$^{207}\text{Pb}/^{204}\text{Pb}$	2SE	$^{208}\text{Pb}/^{204}\text{Pb}$	2SE	$^{207}\text{Pb}/^{206}\text{Pb}$	2SE	$^{208}\text{Pb}/^{206}\text{Pb}$	2SE
<i>Gerard van Honthorst</i>										
SK-A-873_01	18.4756	0.0007	15.6356	0.0011	38.435	0.002	0.84628	0.00005	2.08031	0.00004
SK-A-873_02	18.4684	0.0008	15.6351	0.0013	38.445	0.002	0.84658	0.00006	2.08165	0.00005
SK-A-873_03	18.4798	0.0008	15.6392	0.0013	38.453	0.002	0.84628	0.00005	2.08080	0.00005
SK-A-873_04	18.4770	0.0007	15.6270	0.0013	38.446	0.002	0.84575	0.00005	2.08072	0.00005
SK-A-873_05	18.4878	0.0007	15.6448	0.0012	38.492	0.002	0.84623	0.00006	2.08202	0.00004
SK-A-871_01	18.4830	0.0007	15.6367	0.0012	38.450	0.002	0.84601	0.00005	2.08029	0.00005
SK-A-871_02	18.4773	0.0007	15.6367	0.0011	38.444	0.002	0.84626	0.00005	2.08058	0.00004
SK-A-871_03	18.4809	0.0007	15.6454	0.0012	38.467	0.002	0.84657	0.00005	2.08141	0.00004
SK-A-871_04	18.4878	0.0007	15.6314	0.0013	38.474	0.002	0.84550	0.00006	2.08104	0.00004
SK-A-871_05	18.4751	0.0045	15.6361	0.0038	38.441	0.009	0.84633	0.00007	2.08067	0.00009
<i>Jan van Goyen</i>										
SK-A-120_05	18.4746	0.0014	15.6405	0.0016	38.450	0.003	0.84660	0.00005	2.08120	0.00005
SK-A-120_06	18.4764	0.0008	15.6397	0.0013	38.447	0.002	0.84647	0.00005	2.08086	0.00005
SK-A-120_07	18.4798	0.0009	15.6437	0.0012	38.461	0.002	0.84653	0.00004	2.08120	0.00005
SK-A-120_08	18.4789	0.0008	15.6427	0.0011	38.458	0.002	0.84652	0.00004	2.08114	0.00004
SK-A-120_09	18.4753	0.0010	15.6390	0.0012	38.446	0.003	0.84648	0.00004	2.08093	0.00006
<i>Aert de Gelder</i>										
SK-A-4034-14	18.4633	0.0008	15.6349	0.0012	38.436	0.002	0.84681	0.00005	2.08171	0.00003
SK-A-4034-15	18.4467	0.0008	15.6307	0.0013	38.450	0.002	0.84734	0.00005	2.08437	0.00004
SK-A-4034-16	18.4434	0.0008	15.6313	0.0012	38.459	0.002	0.84753	0.00005	2.08524	0.00003
SK-A-4034-17	18.4466	0.0009	15.6308	0.0012	38.451	0.002	0.84736	0.00005	2.08442	0.00003
SK-A-4034-18	18.4462	0.0008	15.6297	0.0012	38.448	0.002	0.84731	0.00004	2.08431	0.00004
<i>Retouching</i>										
SK-A-4047-19	18.2354	0.0008	15.6208	0.0013	38.196	0.002	0.85662	0.00005	2.09460	0.00004
SK-A-4034-20	18.2294	0.0008	15.6228	0.0013	38.197	0.002	0.85701	0.00005	2.09532	0.00004
SK-A-4047-21	18.2747	0.0008	15.6226	0.0013	38.247	0.002	0.85488	0.00006	2.09285	0.00003
SK-A-4034-22	18.2705	0.0009	15.6267	0.0013	38.247	0.002	0.85530	0.00005	2.09334	0.00003
SK-A-4034-23	18.2481	0.0008	15.6206	0.0012	38.213	0.002	0.85601	0.00005	2.09406	0.00003
<i>Jacob de Gheyn (II)</i>										
SK-A-4255_06	18.4349	0.0007	15.6267	0.0012	38.405	0.002	0.84767	0.00005	2.08323	0.00004
SK-A-4255_07	18.4393	0.0008	15.6334	0.0012	38.425	0.002	0.84783	0.00005	2.08387	0.00005
SK-A-4255_09	18.4290	0.0008	15.6253	0.0013	38.394	0.002	0.84786	0.00006	2.08332	0.00005
SK-A-4255_10	18.4386	0.0017	15.6341	0.0026	38.427	0.006	0.84790	0.00008	2.08401	0.00016
SK-A-4255_13	18.4389	0.0013	15.6352	0.0017	38.430	0.003	0.84795	0.00006	2.08414	0.00006
SK-A-4255_14	18.4361	0.0009	15.6335	0.0015	38.426	0.002	0.84798	0.00006	2.08424	0.00003
SK-A-4255_15	18.4368	0.0010	15.6316	0.0015	38.420	0.002	0.84785	0.00006	2.08382	0.00003
SK-A-4255_17	18.4353	0.0010	15.6318	0.0015	38.419	0.002	0.84793	0.00006	2.08395	0.00003
SK-A-4255_18	18.4353	0.0010	15.6322	0.0018	38.422	0.002	0.84795	0.00008	2.08414	0.00005
<i>micro-scalpel</i>										
SK-A-4255_113a	18.4361	0.0008	15.6297	0.0016	38.414	0.002	0.84778	0.00008	2.08362	0.00005
SK-A-4255_113b	18.4328	0.0008	15.6299	0.0016	38.407	0.002	0.84794	0.00008	2.08362	0.00004
SK-A-4255_113c	18.4158	0.0011	15.6304	0.0020	38.392	0.002	0.84875	0.00010	2.08469	0.00004
SK-A-4255_113d	18.4246	0.0007	15.6284	0.0013	38.400	0.002	0.84824	0.00006	2.08412	0.00004
SK-A-4255_114b	18.4324	0.0008	15.6307	0.0013	38.411	0.002	0.84801	0.00007	2.08388	0.00004
SK-A-4255_114c	18.4283	0.0008	15.6314	0.0017	38.406	0.002	0.84823	0.00008	2.08404	0.00005
SK-A-4255_115a	18.4368	0.0009	15.6310	0.0020	38.416	0.003	0.84781	0.00009	2.08363	0.00007
SK-A-4255_115c	18.4305	0.0008	15.6268	0.0014	38.399	0.002	0.84788	0.00006	2.08343	0.00006
SK-A-4255_117	18.4334	0.0008	15.6281	0.0015	38.407	0.002	0.84782	0.00007	2.08353	0.00005
SK-A-4255_118a	18.4321	0.0009	15.6288	0.0016	38.407	0.002	0.84791	0.00007	2.08370	0.00005
SK-A-4255_119b	18.4303	0.0009	15.6272	0.0014	38.405	0.002	0.84791	0.00006	2.08374	0.00006
SK-A-4255_120c	18.4336	0.0008	15.6302	0.0017	38.413	0.002	0.84792	0.00008	2.08385	0.00006

spectrometers in the early 1990's [23]. Examination of Pb isotope ratio databases of minerals from ore bodies such as OXALID, shows evidence of unresolved mass fractionation effects (e.g., OXALID's Greek data). The study here used the sample standard bracketing (SSB) method to correct for the instrumental mass dependent fractionation. However, the data demonstrate that small mass-dependent effects remain after correction (e.g., Fig. 2g). This is partly a consequence of the inherent instability of the plasma source of an ICP mass spectrometer. Mass-dependent fractionation is the major contribution to the long-term 2SD precision of the analytical method and the main limitation to the resolution of the SSB method. This phenomena causes ~0.015% error in "typical paint analyses" and can be seen in the data from the Venetian lead white cones, where all the analyses are statistically identical but define a slope that is controlled by mass dependent fractionation (Fig. 2g and 2h). It should be noted, however, that compared to the natural variation in Pb-bearing ore minerals, this error is negligible.

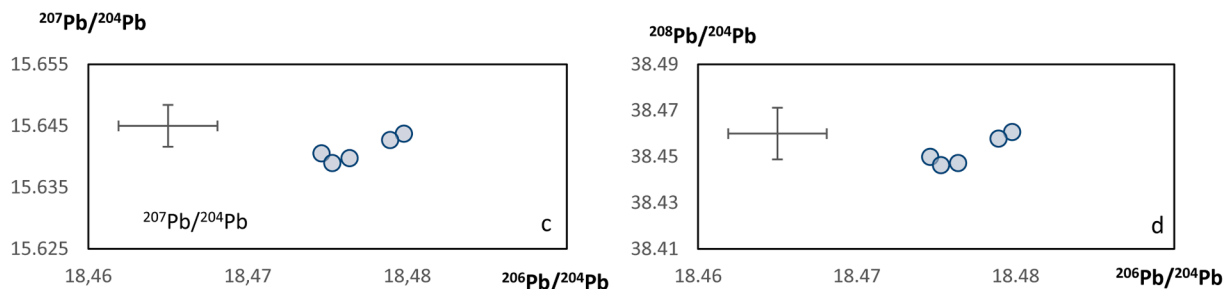
5.1. Lead isotope variance in raw lead white pigment

The Venetian cones (Fig. 2g and h) represent raw lead white pigment produced by the manufacturer for transport to distribution centres. As such, the samples provide a direct indication of the heterogeneity of the "mass produced" product. The seven different cones have variations in $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 1.9, 1.7 and 1.8 times the 2 SD and are thus indistinguishable within analytical uncertainty. There are no systematic isotopic differences between the different cones not sample location within a cone and the samples have a homogeneous Pb isotope composition. This homogeneity is not unexpected, considering new batches of lead white were subjected to several steps of washing and grinding. The method of production and post-production are well described by Homburg (1996) and Stols-Witlox, Megens et al. (2012) [24,25]. The production method described in the papers is referred to as the Dutch stack process, which is only one variant

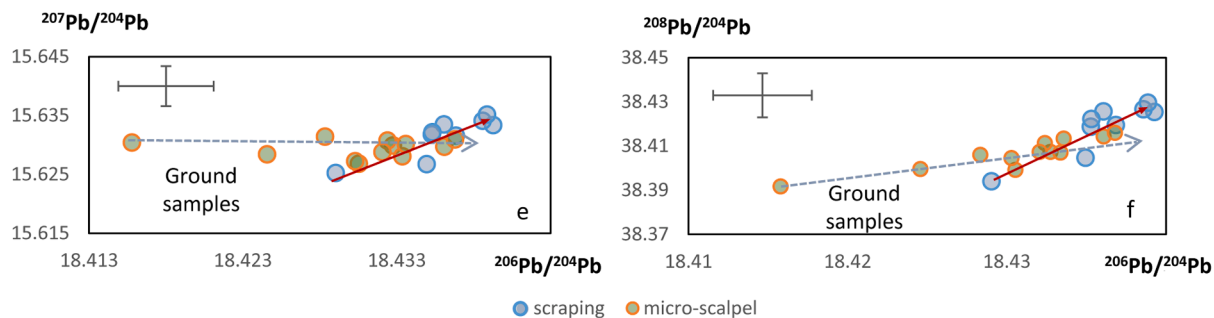
Gerard Van Honthorst



Jan van Goyen



Jacob de Gheyn (II)



Venetian Cones

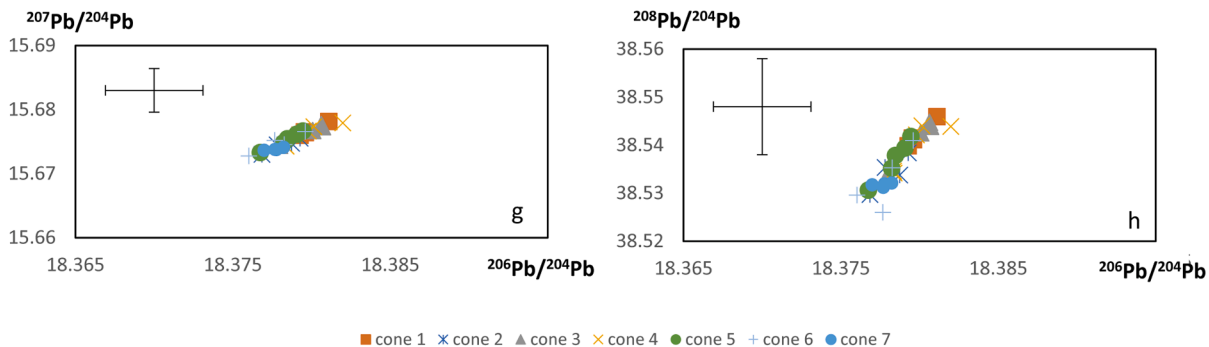
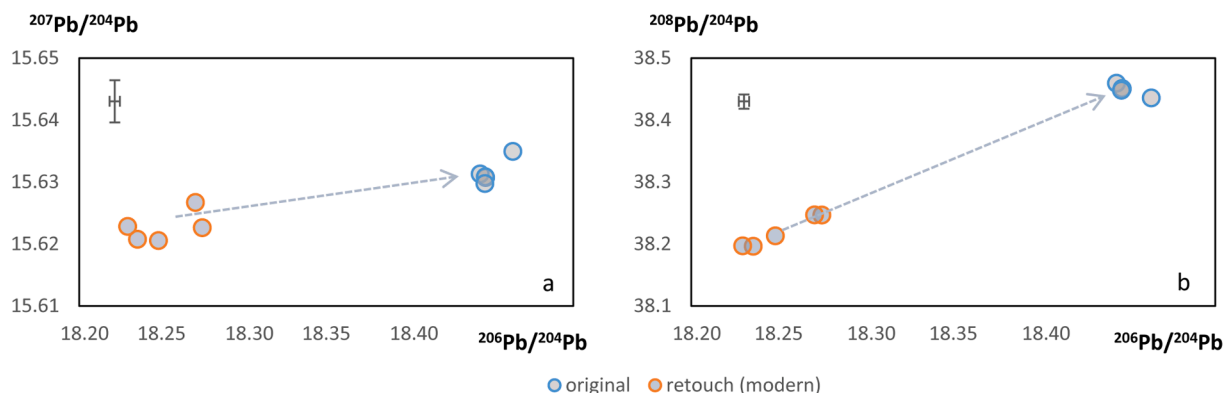


Fig. 2. Pb isotope ratio figures showing results for the samples from: a) and b) the two Van Honthorst paintings; c) and d) results for the samples from van Goyen painting; e) and f) the de Gheyn II paintings. Samples obtained with the two different sampling method are shown with different colours. The two arrow-lines indicate the potential mixing lines of different sources of lead white, one controlled by the ground layer (blue arrow) and one connecting two different sources of lead white (red arrow); g and h) data obtained for the Venetian cones. Each figure includes the long term 2SD precision of the analytical method reported as a cross on the top left.

Retouching and original paint



Original paint

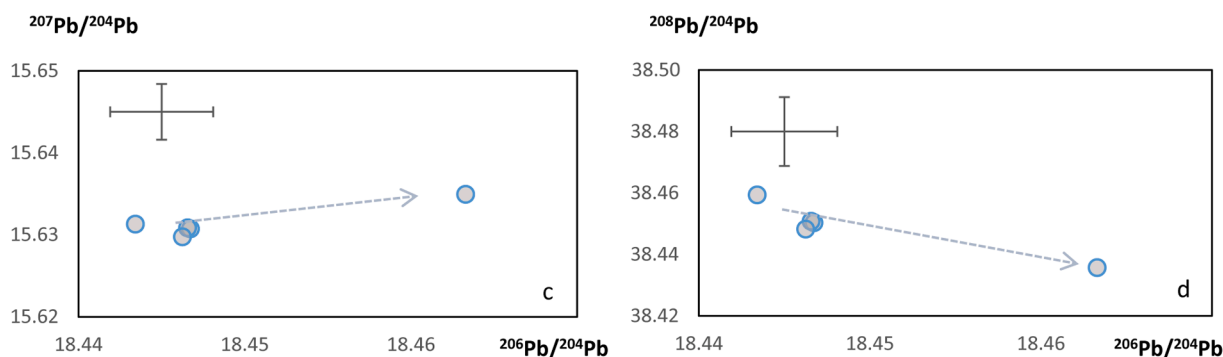


Fig. 3. Pb isotope ratios from the de Gelder painting. a and b) data obtained from the original paint compared with the retouching; c and d) results of the original paint only. The dotted lines indicate potential mixing of different sources. Each graph includes the long term 2SD precision of the analytical method as a cross on the top left of the graph.

of lead white production carried out until the 19th Century. The process can be used as a general example to understand how lead white was produced and treated post-production. Generally, the production of lead white was performed in large batches, starting with the melting of a large quantity of lead that was then transformed to lead white [24,26]. At the peak of the Dutch production, a single lead white producer used 4 tons of lead to start a cycle of production. The first step involves the melting of all metallic lead together and recasting of the melted metal in sheets. After the first step the pigment was processed through many stages of grinding and washing. In this process the pigment was mixed several times in order to obtain a homogeneous product. The initial melting and the post-production steps, in principle, both cause the homogenization of the lead isotopes. Unfortunately, it was impossible to find large quantities of historical lead white Dutch to analyse for this study. However, due to the similarity of production process in lead white over the centuries, it is possible to assume that batches of lead white produced historically were homogeneous, as seen for the Venetian cones. Starting from the assumption of isotopic homogeneity of the raw pigment, any isotopic heterogeneity of lead white found in paintings was introduced during the creation of the paint or a painting. Arguably, the alteration of the isotopic composition of lead white could have happened when pigments were mixed with other substances, containing contaminants (oils, varnishes, extenders and other pigments). In summary, based on the homogeneity of the raw material analysed here, the isotopic data suggest that any increase in the level of isotopic heterogeneity in the lead white paint can be ascribed to processing of the pigment that happened after trading.

5.2. Lead isotope variation in 17th century Dutch paintings

Lead isotope data from the Gerard van Honthorst painting SK-A-871 vary by 4.1 times the 2SD for both $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ and 3 times for $^{208}\text{Pb}/^{204}\text{Pb}$ (Table 2, Fig. 2a and b). In the companion painting, SK-A-873, the same Pb isotope ratios vary by 6.2, 5.3 and 5.1 times 2SD respectively. In contrast to the data for the lead white cones, the samples of these two paintings have values outside analytical uncertainty and overall have variations in $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 6.3, 5.9 and 5.1 times 2SD respectively. The similar average isotopic composition of the two paintings reinforces the hypothesis that a common batch of lead white was used to prepare these two works. The isotopic heterogeneity found in the two paintings suggests, however, that the lead white comprised a poorly homogenized combination of different lead whites or a combination of lead white with some lead-bearing material or lead-rich paint medium. This observation supports the hypothesis that the lead isotope ratios of lead white can be altered in the process of painting.

Samples of the Jan van Goyen painting (SK-A 120, Fig. 2c and d) have Pb isotope ratios that are indistinguishable within analytical uncertainty, with $^{206}\text{Pb}/^{204}\text{Pb}$ ratios equal to 2 2SD, 1.7 2SD for $^{207}\text{Pb}/^{204}\text{Pb}$ and 1.3 for $^{208}\text{Pb}/^{204}\text{Pb}$. In contrast, samples analysed from the Aert de Gelder painting (SK-A-4034) divide into two clusters (Table 2, Fig. 3a and b). The retouching is more heterogeneous with the variation in $^{206}\text{Pb}/^{204}\text{Pb}$ ratio equal to 14.8 times 2SD. These Pb isotope ratios are comparable to some lead white produced after the 18th century and significantly distinct from 17th century Dutch paintings [4].

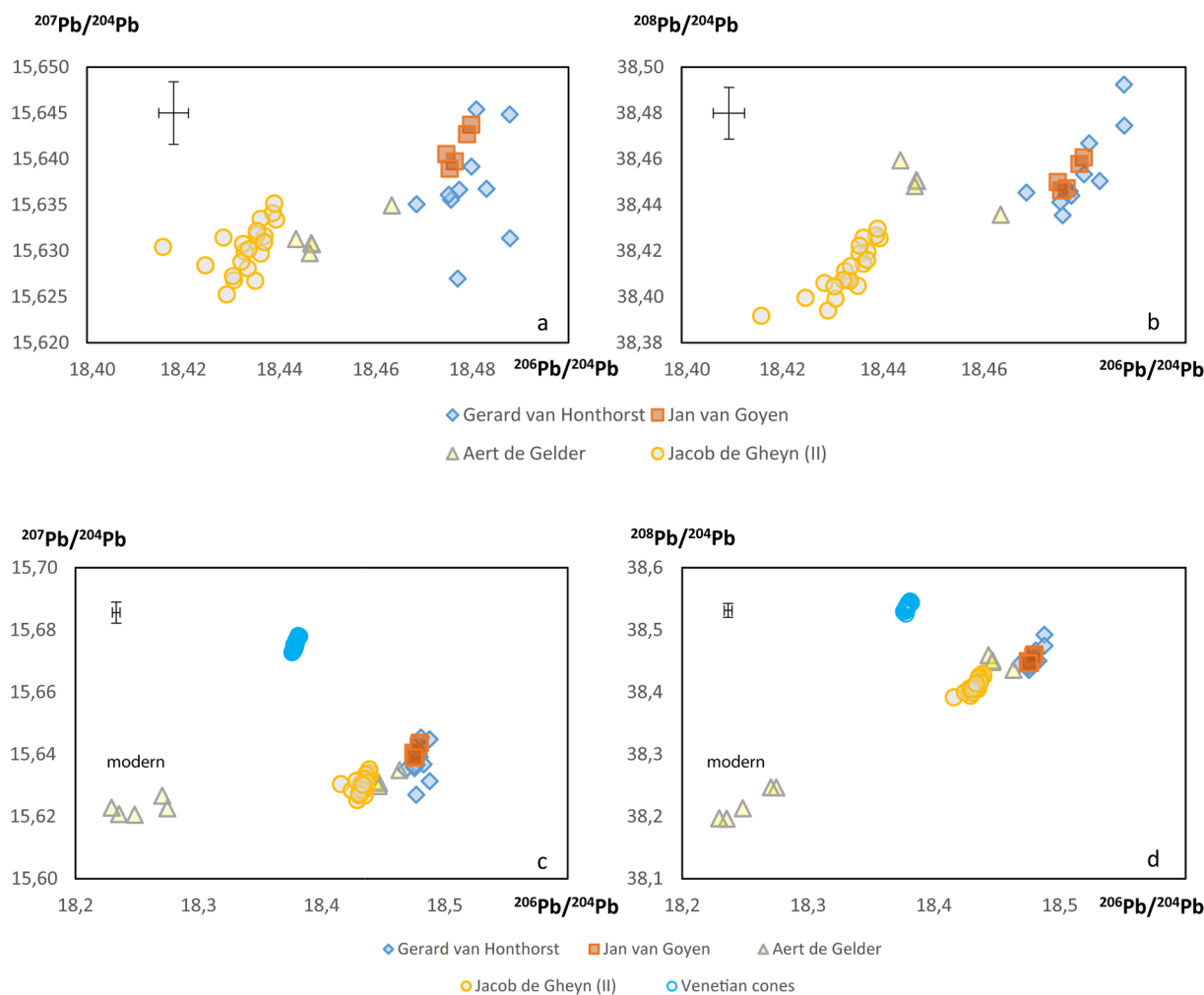


Fig. 4. a and b) Pb isotope ratios from all the paintings; c and d) comparison of data obtained for the Dutch paintings with Venetian lead white cones and the retouching present in the de Gelder painting.

The high variability of the isotopic data from the retouched paint is notable and suggests that the restoration of the painting either involved different paints, possibly at different periods or that, more likely, the modern lead white is partly mixed with the original 17th century lead white. The latter scenario is supported as the samples lie on a two-component mixing line connecting the original isotopic values to the modern values (dotted arrows, Fig. 3a and b). The total isotopic variation for the original 17th-century paint in $^{206}\text{Pb}/^{204}\text{Pb}$ is comparable to that found for the van Honthorst's paintings (Fig. 3c and d). Four of the original samples are statistically identical, while one (ID: SK-A-4034-14) is different by 6 times 2SD in $^{206}\text{Pb}/^{204}\text{Pb}$ (Fig. 2d). The $^{207}\text{Pb}/^{204}\text{Pb}$ ratio values are indistinguishable while the $^{208}\text{Pb}/^{204}\text{Pb}$ is just outside analytical error (2.1 2SD). The observed isotopic variability can be explained by contamination of sample SK-A-4034-14 with some other Pb-containing pigment present in the painting or the use of two lead white pigments containing different Pb (arrows in Fig. 3c and d). More analyses are required to establish if the two components were used separately, or as mixtures, as in the van Honthorst painting.

Lead isotope ratios of lead white from Jacob de Gheyn (II) vary by 7.6 times 2SD for $^{206}\text{Pb}/^{204}\text{Pb}$, 2.6 for $^{207}\text{Pb}/^{204}\text{Pb}$ and 3.4 for $^{208}\text{Pb}/^{204}\text{Pb}$ (Table 2, Fig. 2e and f). The variability in $^{206}\text{Pb}/^{204}\text{Pb}$ ratio is primarily a result of the compositions of sample SK-A-4255_113c. This sample was taken using a micro scalpel and is one of four samples where a particle of lead white was extracted from the ground layer. Another sample, SK-A-4255_113d, was also taken from the ground layer. The results for the latter fall between the values of sample SK-A-4255_113c

and the rest of the samples. The difference of these samples from the rest of the group could be caused by mixing with impurities present within the ground layer. If the two ground layer samples are not considered, the variation in the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio for the remaining samples is reduced but is still significant, 3.5 times the 2SD. Note that the data do not record a systematic division between samples coming from different layers of the painting. The isotopic homogeneity of the mass produced Venetian lead white indicates that the level of heterogeneity in these samples must be the results of the preparation of the lead white during the painting process. The data further suggest mixing involving three components, one component is defined by the ground layer and two are defined by the remaining samples (arrows in Fig. 2e and f). This again suggests that the lead white used was either a poorly homogenized combination of slightly different lead whites or that some lead white contains lead impurities from other sources.

Overall four of the five 17th-century Dutch paintings contain lead white with variable Pb isotope ratios. Samples of lead white from the Van Goyen are the only example isotopic homogeneity. For the other four paintings two different observations are made. First, lead white from an individual painting forms a "continuous" cluster of data that is larger than analytical uncertainty (as for the samples from de Gheyn (II) and Van Honthorst). Secondly, the data may contain a single or multiple analyses that suggest the presence of distinct lead components. The data collected from de Gheyn (II) and de Gelder, for example, suggest that the lead white in these paintings was a mixture of two or three components containing different Pb isotope ratios and that the components were not

Table 3

Results of the Venetian cones samples with two times the standard error, 2SE.

Venetian cones	$^{206}\text{Pb}/^{204}\text{Pb}$	2SE	$^{207}\text{Pb}/^{204}\text{Pb}$	2SE	$^{208}\text{Pb}/^{204}\text{Pb}$	2SE	$^{207}\text{Pb}/^{206}\text{Pb}$	2SE	$^{208}\text{Pb}/^{206}\text{Pb}$	2SE
<i>cone 1</i>										
a451	18.3811	0.0007	15.6781	0.0011	38.546	0.002	0.85295	0.00004	2.09702	0.00004
a452	18.3796	0.0006	15.6764	0.0010	38.541	0.001	0.85293	0.00004	2.09693	0.00003
a453	18.3795	0.0006	15.6765	0.0010	38.541	0.001	0.85294	0.00004	2.09695	0.00003
a454	18.3793	0.0006	15.6760	0.0011	38.540	0.001	0.85292	0.00005	2.09689	0.00003
<i>cone 2</i>										
a457	18.3787	0.0007	15.6747	0.0011	38.534	0.002	0.85287	0.00005	2.09662	0.00004
a458	18.3768	0.0006	15.6730	0.0011	38.530	0.002	0.85287	0.00005	2.09662	0.00004
a459	18.3778	0.0006	15.6745	0.0010	38.535	0.001	0.85290	0.00005	2.09681	0.00003
a460	18.3793	0.0006	15.6755	0.0012	38.538	0.001	0.85289	0.00005	2.09681	0.00003
<i>cone 3</i>										
a461	18.3801	0.0007	15.6767	0.0012	38.543	0.002	0.85292	0.00005	2.09695	0.00004
a462	18.3806	0.0008	15.6777	0.0012	38.545	0.002	0.85295	0.00005	2.09701	0.00005
a463	18.3780	0.0008	15.6744	0.0015	38.534	0.002	0.85289	0.00006	2.09672	0.00004
a465	18.3807	0.0007	15.6773	0.0012	38.544	0.002	0.85292	0.00005	2.09695	0.00003
<i>cone 4</i>										
a466	18.3820	0.0009	15.6779	0.0012	38.544	0.002	0.85290	0.00005	2.09680	0.00003
a467	18.3801	0.0006	15.6773	0.0010	38.544	0.001	0.85295	0.00004	2.09702	0.00003
a468	18.3783	0.0006	15.6744	0.0011	38.535	0.001	0.85287	0.00005	2.09671	0.00003
a469	18.3798	0.0006	15.6766	0.0011	38.542	0.001	0.85293	0.00005	2.09696	0.00003
a470	18.3784	0.0006	15.6743	0.0011	38.534	0.001	0.85287	0.00005	2.09669	0.00003
<i>cone 5</i>										
a471	18.3767	0.0007	15.6733	0.0011	38.531	0.002	0.85289	0.00005	2.09668	0.00003
a472	18.3782	0.0007	15.6748	0.0013	38.535	0.002	0.85290	0.00006	2.09676	0.00003
a473	18.3794	0.0007	15.6767	0.0012	38.542	0.002	0.85295	0.00005	2.09698	0.00003
a474	18.3791	0.0007	15.6761	0.0012	38.539	0.002	0.85294	0.00005	2.09689	0.00003
a475	18.3785	0.0006	15.6755	0.0011	38.538	0.001	0.85293	0.00005	2.09688	0.00003
<i>cone 6</i>										
a476	18.3796	0.0006	15.6766	0.0012	38.541	0.001	0.85293	0.00005	2.09692	0.00003
a477	18.3777	0.0006	15.6752	0.0011	38.526	0.001	0.85287	0.00005	2.09656	0.00003
a478	18.3783	0.0006	15.6745	0.0011	38.535	0.001	0.85289	0.00004	2.09676	0.00003
a480	18.3760	0.0007	15.6728	0.0011	38.530	0.002	0.85289	0.00004	2.09670	0.00003
<i>cone 7</i>										
a482	18.3770	0.0007	15.6736	0.0011	38.532	0.002	0.85290	0.00004	2.09671	0.00003
a483	18.3782	0.0008	15.6741	0.0011	38.532	0.002	0.85286	0.00004	2.09659	0.00004
a484	18.3777	0.0007	15.6738	0.0011	38.531	0.002	0.85287	0.00005	2.09660	0.00004
a485	18.3778	0.0007	15.6737	0.0010	38.532	0.002	0.85287	0.00004	2.09663	0.00004

mixed efficiently. The identification of two or three different components raises questions as to the modus operandi of the artists. Are the isotopic differences the result of the mixing of different batches of lead white in the artist workshop, possibly reflecting recycling of old and new lead white to save on material costs? In order to resolve this issue a more extensive systematic study is required. Based on the results so far, we can say that heterogeneity of lead isotopes in lead white within a single painting is an recurring phenomenon, therefore this aspect should be considered when decisions on sampling locations are made for these types of investigations. The results show, in particular, the need of multi-sampling strategy for a single painting when lead isotopes analyses are required.

5.3. Implication of Pb isotope variation.

The Pb isotope data combined in one diagram define three main clusters (Fig. 4a and b): the Venetian cones, the retouching on the Aert de Gelder and the 17th-century Dutch paintings. The Venetian cones have Pb isotope ratios that correspond with those of 16th-century Italian paintings [5]. The cones are clearly manufactured using lead ores from a different source to that used for Dutch paintings and are consistent with north-Italian paintings [4,5]. The Dutch paintings presented here have Pb isotope data comparable to the data reported by Fabian and Fortunato 2010 [5], identified in 17th-century Dutch paintings between 18.41 and 18.48 and 15.61–15.64 for $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, respectively. This range is defined by two sub-groups in Fig. 4c and d: one formed by Van Honthorst, Van Goyen and one sample from the De Gelder on the right, and lead white from de Gheyn II and de Gelder on the left. In the $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{208}\text{Pb}/^{204}\text{Pb}$ Fig. 4d, three clusters can be observed and it is possible to distinguish the four samples from the De

Gelder from the cluster formed by the De Gheyn. The samples from Van Honthorst and Van Goyen are within analytical uncertainty of samples of lead white from Vermeer's *Girl with the pearl earring* and some Frans Hals [6,7].

The distribution of lead isotopes suggests that a single Pb source was dominant in lead white manufacture in the region during the 1650/1660 period. Moreover, the Pb isotope signature of the lead white of this period is statistically distinct to the lead white used in the same region at the beginning of the 17th century (De Gheyn II) and at the beginning of the 18th century (De Gelder). The isotopic variation of lead white for these paintings suggests temporal variation of the lead used to manufacture lead white in the Netherlands. England was the main lead producer at these time [27] and the isotopic ratios are consistent with a UK origin [7]. The observed isotopic variations suggest that potentially English lead production and export was disrupted by the English civil war of 1641–1652. Further work is, however, required to substantiate this supposition.

Consideration of the variation of lead isotope ratios in lead white within the 17th-century Dutch samples shows individual paintings as statistically different (e.g., de Gheyn II and van Honthorst), whereas samples from other artists are indistinguishable. This observation emphasises the need for a detailed lead isotope ratio database to fully understand potential temporal isotopic variations in lead white. The fabrication of such a database is crucial in order to interpret correctly the results of lead isotope analyses, and only in this way could art-historians and curators use Pb isotope variations in order to determine the provenance of the pigment or have evidence to support attribution of the paintings.

6. Conclusion

The study determined the homogeneity of lead isotope ratios of commercially produced Venetian lead white pigment. The results demonstrate that individual shipments of pigment were isotopically homogeneous. The analyses of the lead isotopes of lead white in samples from 17th-century Netherlandish paintings, however, show that four out of five paintings contain lead white samples that are statistically different. Based on the homogeneity found in the pure lead white pigments, the isotopic heterogeneity is interpreted as the result of pigment processing and use in the artist's studio prior to painting. The most plausible hypothesis to explain this isotopic heterogeneity is mixing of different generations of lead whites, or the contamination of the lead white with other Pb-bearing materials. These findings suggest that future lead isotopes analyses on lead white on paintings should be conducted following a multi-sampling strategy, in order to fully assess the lead isotope heterogeneity for the studied painting. Moreover, the study suggest that, due to lead isotope heterogeneity, a larger database is fundamental for comprehensive data interpretation.

This work, in accordance with literature data, finds a clear separation of lead isotope ratios from different artistic periods, and three groups were identified: Venetian cones, 17th century Dutch paintings and modern lead white. Dutch paintings suggest an isotopic difference between samples from the middle of the 17th century and the beginning of the 17th and 18th centuries. These preliminary Pb isotope data suggest a time-dependent variation in the Pb ores used in lead white but calls for a more detailed and systematic study of 17th-century Dutch paintings.

CRedit authorship contribution statement

Paolo D'imporzano: Conceptualization, Methodology, Formal analysis, Data curation, Writing - original draft, Writing - review & editing. **Katarina Batur:** Resources, Writing - review & editing. **Katrien Keune:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision. **Janne M. Koornneef:** Conceptualization, Data curation, Writing - review & editing, Supervision. **Erma Hermens:** Conceptualization, Resources, Writing - review & editing, Supervision. **Petria Noble:** Conceptualization, Resources, Writing - review & editing, Supervision. **Kirsten Zuilen:** Methodology, Data curation, Writing - review & editing. **Gareth R. Davies:** Conceptualization, Methodology, Data curation, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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