

# Chapter 14

## Lead Isotope Ratios of Lead White: From Provenance to Authentication



Paolo D'Imporzano and Gareth R. Davies

**Abstract** The chapter reports the latest developments on the use of lead isotope analysis in the field of painting study, highlighting the contribution that this technique can bring to authentication of paintings and forgery detection. The chapter discusses the state of the art and the novel applications of lead isotope analysis to characterise paintings, using a detailed study of seventeenth century Dutch paintings as an example. Topics covered include: pigment/paintings provenance, regional isotopic variation, time-dependant lead isotope ratio variation and the travel of artists. Determining lead isotope ratio variation contributes to an increased understanding of paint-making, adding new and necessary knowledge useful for painting authentication. The work presented will help the reader understand the great potential contribution of lead isotope analysis to cultural heritage.

**Keywords** Lead isotope ratios · Analytical methods · Lead white · Provenance

### 14.1 Introduction

Is it possible to identify a forged painting by using the lead isotope ratios of lead white? As usual, the answer to such a relatively simple question is not definitive: yes, but it depends. Lead isotope analysis of lead white is a technique that has been used since the 1970s in order to identify the isotopic composition of the pigment (Keisch and Callahan 1976). In initial studies, the focus was on tracking the provenance of the lead used to produce lead white. In subsequent decades, associated with the development of more sensitive mass spectrometry, this technique also contributed to studies focusing on characterisation of artistic periods based on their lead white isotopic signature (Fabian and Fortunato 2010; Fortunato et al. 2005; Hendriks

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et al. 2020). In these latter studies, however, the bulk of the isotopic data were obtained from sixteenth to seventeenth century Italian or Netherlandish painters, meaning that many important artistic periods and regions have yet to be characterised.

The use of lead isotope ratios for identification of a painting's source or age is not straight forward and requires knowledge on several factors that influence the production of the painting and the production of the pigment. The latter needs knowledge of the source and nature of the smelting process used to extract the raw materials and how metallic lead is traded and processed prior to the paint production process. It is perhaps correct to conclude that the several days preparation to perform isotopic analyses of lead white is, arguably, the easiest part for the characterisation of the pigment. Information about which mines were active, which trade routes were used, in which region or time the painting was produced are fundamental in order to be able to use lead isotope data for authentication or attribution. Once these conditions are met then undoubtedly it is possible to use lead isotope ratios to distinguish certain groups of paintings, and use this information for attribution, authentication or even to detect later modification and potentially forgeries. This chapter will outline how lead isotope analyses of lead white are undertaken and how the data can be interpreted. Initially background information is provided on how lead white was produced, traded and used and a brief review of the analytical technique is also given. How the technique can be applied and the limitations will focus on the seventeenth century, with special attention to Dutch painters, as this period has been the most extensively studied and provides the best database to consider the potential of lead isotope analysis for authentication or attribution.

## 14.2 Lead White Production

Lead white almost invariably consists predominantly of a mixture of two lead carbonates: (C) cerussite ( $\text{PbCO}_3$ ) and (HC) hydrocerussite ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ) (Olby 1966). Other lead salts such as plumbonacrite ( $\text{Pb}_5\text{O}(\text{OH})_2(\text{CO}_3)_3$ ) are rare but have been reported in a number of synchrotron studies and appear to be a function of the ambient pH during paint production (Gonzalez et al. 2019; Stols-Witlox et al. 2012; Welcomme et al. 2007). The high content of lead ( $\sim 77\text{--}80\%$  by weight depending upon the C/HC ratio in the pigment) makes lead white the perfect candidate for lead isotope analysis. Coupled with the quasi-ubiquitous presence of this pigment in every painting until the twentieth century, it is possible to examine how paintings clusters based on painter, geography or time.

Lead white has been used as a pigment since before ancient Egyptian (Walter et al. 1999) and the synthesis of the pigment has not changed significantly over time. Detailed written description of its use were given during Roman times by

Theophrastus (fourth century B.C.), Vitruvius (first century B.C.) and Pliny the elder (first century A.D.)<sup>1</sup> (Eastaugh et al. 2004; Welcomme, 2007).

Lead white production consists of the transformation of metallic lead to a carbonate by exposure to acetic acid vapours (vinegar) in a fermentation medium (typically horse manure). Venice was the main production centre for this pigment from the twelfth until the sixteenth century (Berrie and Matthew 2011). The pigment was produced directly in the city, and enormous quantities of metallic lead were transported and processed in Venice. Documents report that in Venice, at least one lead foundry and one lead white factory ('luogo dale sbiacche'), as well as a shop specially dedicated to the sale of lead white ('la botega dalle sbiacche et altro posta sopra el ponte di Rialto') were active in the sixteenth to seventeenth century (Berrie and Matthew 2011). At the end of the sixteenth century, lead white production was implemented by Dutch craftsmen on a commercial scale and the production of the pigment increased in order to meet a constantly increasing demand. In this period the main production centre for lead white became the Netherlands, which would maintain this position until the 1800s. The rise of the Dutch industry was initiated at the end of the sixteenth century when the fall of Antwerp to the Spanish in 1585 forced many craftsmen to move north toward the Netherlands where they created the basis of the lead white industry in the country (Homburg and de Vlieger 1996). Producers in the Netherlands managed to improve the efficiency and increase the scale of the production process. This was achieved by using thin coils of metallic lead that were placed into pots with vinegar and staked in successive layers. The innovation was that the metallic lead coil increased the active surface area. In addition, the reaction time was increased to maximise acid attack of the lead sheets. The synthesis process reached quasi-industrialised productivity yielding large quantities (tons) of lead white. This improved process led to a production boom in Holland, and it became common to refer to the process as the Dutch stack process (Homburg and de Vlieger 1996). From the end of the sixteenth century, the Dutch started to produce and trade lead white on a large scale, becoming the main production centre in the seventeenth and eighteenth century (Stols-Witlox 2014). The details of the Dutch stack process are well explained by Homburgh (Homburg and de Vlieger 1996), and references within, and this work can be taken as a reference of lead white production until the nineteenth century. Records suggest that at the peak of the activity, a single lead white producer was able to process four tons of lead in a single production batch. The process started by melting together the metallic lead, which included mixing new and unreacted metallic lead recycled from previous lead white production. The lead was then cast into metallic sheets (or in thin lead coil in the Dutch stack process) and exposed to vinegar under a CO<sub>2</sub>-rich atmosphere. The process to convert metallic lead into lead white required 6 to 8 weeks, depending on the ambient temperature and humidity. After conversion of the metallic lead, the pigment was washed and ground several times according to various recipes in order

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<sup>1</sup>Theophrastus, *De lapidibus*, 56; Vitruvius, *De Architectura*, 8, 6, 1; Pliny the old, *Histoire Naturelle*, 34, 175.

to obtain the desired final grain size and purity (Stols-Witlox et al. 2012). After a final drying step, the product was ready to be sold. Documentary evidence indicates that lead white produced in the north of Europe could be mixed with chalk ( $\text{CaCO}_3$ ) in order to cut the production cost, whereas the lead white from Venice was known to be pure and considered of a higher quality (Berrie and Matthew 2011; Homburg and de Vlieger 1996; Stols-Witlox et al. 2012). This fact allowed Venetian lead white to maintain a position as a high quality product on the international lead white market, which was dominated by the Dutch in the seventeenth century. It is estimated that in 1790, 1350 tons of lead white were shipped out the harbours of Amsterdam and Rotterdam (Stols-Witlox 2014; Vlieger and Homburg 1992) and that at the end of the eighteenth century more than 35 factories were active in the Netherlands with a production of 4000 tons per year.

Lead white is not the only lead based pigment produced, but it is the only one that has been well-characterised with lead isotope analysis. The other notable lead based pigments used in history are: minium ( $\text{Pb}_3\text{O}_4$ ), lead thin yellow ( $\text{Pb}_2\text{SnO}_4$ ), Naples yellow ( $\text{Pb}_2\text{Sb}_2\text{O}_7$ ) used between eighteenth and nineteenth century and chrome yellow ( $\text{PbCrO}_4$  used from the nineteenth century) (Feller 1986; Roy 1993). These pigments, however, have not been studied as much as lead white and, therefore, their isotopic compositions remain unknown.

Knowing the production process and the trading of the lead white is fundamental for lead isotope data interpretation. The implication of the commercial production is that large quantities of lead white were produced at one time from lead that was melted and hence homogenised before being re-casted into the required shape. The lead used was either new or recycled from previous production batches, meaning that potentially different sources of lead were mixed together. This suggests that the final lead white product should be isotopically homogenous due to rapid diffusion of the element within a melt and due to physical mixing during the processes of grinding and washings after the lead was transformed in lead white. Depending on variations in the amount of recycled lead used, each lead white batch could potentially have a different isotopic composition. This conclusion is due, not only to the recycling of lead but also to changes in lead isotope composition of individual lead ore deposits during their progressive exploitation or changes in the supply chain of lead ore. Although Dutch lead white, was adulterated with chalk, the difference in lead content ( $\sim 77\text{--}80$  wt. % Pb in lead white compared to less than 10 ppm in chalk) means that adulteration is expected to have minimal effect on the final lead isotope composition.

### 14.3 Lead Ore Deposits

Large quantities of lead commonly occur in ore deposits in association with zinc and less commonly with copper and iron. In all cases these elements occur in sulphide minerals that were formed by precipitation from ore fluids due to processes such as cooling, mixing with other fluids, and pH change. The most common

sulphide minerals are galena (PbS, 87 wt.% Pb), sphalerite (ZnS), chalcopyrite (CuFeS<sub>2</sub>), pyrite(FeS<sub>2</sub>), and pyrrhotite (FeS). The largest mineralised regions can contain up to  $10 \times 10^6$  tons (t) of Pb, in addition to the other metals.

Significant lead accumulations occur in oceanic and continental crust in seven main types of ore deposits that are conventionally grouped based on geological occurrence (Eckstrand et al. 1995). Skarn and manto deposits are hosted in carbonate rocks and associated with igneous intrusive bodies such as granite. Fluids expelled during cooling of the igneous bodies reacted with, and replaced, the carbonate rocks precipitating sulphides. Skarn deposits were formed at high temperatures (>350 °C) associated with formation of calcium silicate minerals. Manto deposits form further from the igneous bodies and lack the distinctive calcium silicate assemblage. Both deposit-types form large, “massive” (i.e., typically >60% sulphide) deposits containing mainly Pb and Zn sulphides, although silver is commonly an important by-product. Mississippi Valley-type (MVT) deposits are also hosted in sedimentary carbonate rocks and named after three mineralised regions in the Mississippi Valley, USA, although other large MVT sphalerite and galena deposits with low pyrite content occur world-wide. They formed due to the tectonically driven expulsion of metal sulphide-rich hydrothermal fluids from shale into surrounding carbonate rocks. Igneous intrusions were not involved and depositional temperatures were lower than manto and skarn type deposits (100–150 °C). Deposits are normally Zn-rich and the silver content is low. MVT deposits generally occur as clusters ranging from a few to more than 300 separate deposits.

Volcanogenic massive sulphide (VMS) deposits are found in volcanic rocks as old as 3.5 billion years and are still forming at mid ocean ridges today. The deposits commonly contain Cu, Pb, Zn, Ag and Au. Although VMS deposits form in variable geological environments, all form by metals being leached from the surrounding sub-seafloor volcanic rocks by seawater circulating in a hydrothermal system. Sulphides precipitate on or near the seafloor due to changes in temperature, pressure, and pH when the rising hydrothermal fluids interact with seawater. Sedimentary-exhalative (SEDEX) deposits represent the largest known Pb and Zn deposits with several containing in excess of  $10 \times 10^6$  t of metal. SEDEX deposits were formed close to the seafloor by seawater circulating through underlying sediments. The deposits are bi-mineralic, sphalerite and galena with highly variable Ag contents, 0 to ~300 g/t. Sandstone-lead deposits do not represent major sources of Pb on a world scale but were the major source of Pb in Sweden and Germany. Galena, usually accompanied by lesser amounts of pyrite or sphalerite, is disseminated within sandstone at relatively low ore grades. The sedimentary sandstone host rock usually overlies older rocks of granitic composition, which are the source of the Pb. The final lead occurrence is vein deposits. Veins formed in a series of narrow fractures, cutting through the host rock and filled with ore minerals that precipitated from hydrothermal fluids. Lead-bearing veins are associated with a variety of sulphides, Ag-bearing minerals, quartz, and calcite. Although generally small compared with the other deposits, vein deposits have been exploited from prehistoric up to the nineteenth century.

## 14.4 The Isotopes of Lead

Lead has four stable isotopes,  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ .  $^{204}\text{Pb}$  is non radiogenic while  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  are the product of radioactive decay of respectively  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$ . The decay rates of the parent isotopes differ by more than a factor of 10.  $^{232}\text{Th}$  has the slowest decay with a half-life of  $1.4 \times 10^{10}$  y. The half-life of  $^{238}\text{U}$ ,  $4.47 \times 10^9$  y, is comparable to the age of the Earth whereas the half-life of  $^{235}\text{U}$  is almost seven times shorter ( $7.07 \times 10^8$  y) such that the vast majority (> 95%) of  $^{235}\text{U}$  has now decayed away. This means that the rate of change in the ingrowth of the daughter Pb isotopes has changed significantly over time with notably more  $^{207}\text{Pb}$  formed during early Earth evolution. Rocks formed in the Achaean period therefore had notably higher  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios. Galena contains such large amounts of Pb that it has U/Pb and Th/Pb ratios close to zero so that once formed, there is no change in the Pb isotope ratios in galena. This means that the Pb isotope ratios are “frozen” at the time of formation and represent a record of the Pb isotope ratio at that time. Lead ore deposits formed in different geological periods therefore generally have distinct Pb isotope ratios.

Lead ore deposits are formed from lead derived from two major sources: (i) the continental crust that is enriched in U and Th such that the crust is characterised by elevated (radiogenic) Pb isotope ratios or (ii) Earth's upper mantle, either directly or from recently formed lower continental crust. Earth's mantle has a predictable Pb isotope compositions with time that approximately follows a two stage evolution model (Galer and Goldstein 1996; Stacey and Kramers 1975). In this model, Pb develops from primordial Pb, defined by troilite recovered from meteorites with  $^{238}\text{U}/^{204}\text{Pb}$  and  $^{232}\text{Th}/^{204}\text{Pb}$  of 7.19 and 32.21 respectively. Following a major differentiation event at 3.7 Ga,  $^{238}\text{U}/^{204}\text{Pb}$  and  $^{232}\text{Th}/^{204}\text{Pb}$  increased to 9.74 and 37.19. Many ore bodies have compositions that approximate the mantle evolution model and have been variously described as ordinary or common (Pollard and Heron 2008). In these cases, there is little contribution of radiogenic lead from the upper continental crust. A second group of lead deposits, described as anomalous, indicate the involvement of lead sources derived from continental crust of different age (Gulson 1986; Sangster et al. 2000).

All the factors described above contribute to the understanding of the nature and timing of the processes that form lead deposit, and make it possible to use the Pb isotope system to determine Pb provenance in cultural heritage studies. Common lead deposits formed in the same period, will have the same Pb isotope composition, even if the geographical regions of the two deposits are distant. In contrast, anomalous deposits may have distinct isotopic compositions even if they are formed in close proximity. This characteristic of lead deposits is what makes the Pb isotope system so powerful for provenance studies as potentially most ore deposits have a distinct signature.

Within Europe, however, ore deposits often formed in regions with similar geological backgrounds and histories (Germany, Poland and U.K). Nevertheless, even in these areas it is possible to distinguish ore bodies formed in local regions. Hence,

if the exploitation history of individual ore deposits is known, Pb isotope compositions can be used to determine the provenance of lead in cultural heritage objects.

## 14.5 Lead Production

Lead, due to its low melting point and association with silver was one of the first metals to be smelted by humans. Since antiquity lead extraction from galena (PbS) was almost ubiquitously connected with silver recovery, and many silver-rich lead deposits were used in order to obtain the precious metal. For many centuries lead was considered a by-product of silver production and the usefulness of metallic lead was not widely recognised (Henderson 2013). The first documented trade in lead was recorded in an inscription found in a temple from the 18th Egyptian dynasty (~3400 BP). The use of lead from that time onwards is documented in ice cores from Greenland, where lead pollution is recorded at concentrations four times higher than previously (Hong et al. 1994). Peaks in lead pollution are dated at 2500 and 1700 years ago, which coincides with mining and smelting activity at the height of Greek and Roman societies. The peak of pollution due to the processing of lead during the Roman period was not reached again until the industrial revolution (Cooke and Bindler 2015; Hong et al. 1994). During Greco-Roman times, lead mining and processing were most active in Spain, which represented around 40% of production of the Roman Empire with significant production in Central Europe, Britain, Greece and Asia minor (Cooke and Bindler 2015; Fortunato et al. 2005; Hong et al. 1994; Pollard and Heron 2008; Stos-Gale and Gale 2009).

Detailed lead pollution records obtained from European lakes have been used to indicate that the use of lead after the decline of the Roman Empire decreased considerably and only started to rise again around 1000 years ago (Cooke and Bindler 2015). From this time on, the lead contents of lake sediments closely correlate with lead production in Europe. By the eleventh and twelfth century, many old Roman lead production centres had re-opened in Germany, Britain and Spain. By the sixteenth century the main lead production centres were Germany, Poland and U.K., with the latter becoming the world leading lead producer in the seventeenth century.

During the industrial revolution lead production exceeded that of the Roman Empire. Britain was no longer the leading lead production centre by the mid-nineteenth century, in association with the depletion of its mines and the re-development of lead mining in Germany, Spain, and major expansion in the United States. In the same period major lead deposits were discovered in Australia. The United States became the leading global lead producer at the end of the nineteenth century, and associated with increasing production from other non-European nations such as Canada, Mexico, and Australia, non-European lead production surpassed European mines (Rich 1994). Today, Australia is the world's leading producer and exporter of lead, with large mines at Broken Hill, Mt Isa and Hilton in Queensland and McArthur River in the Northern Territory. In deposits mined today, lead is usually found in ores which also contain zinc, silver and commonly copper and is

extracted as a co-product of these metals. Much of this lead production is from regions characterised by ancient geology (1.0–3.0 Billion years old) and has characteristic lead isotope ratios. Lead sulphide, the major ore mineral, contains insignificant amounts of U and Th and hence undergoes essentially no radioactive decay after formation. As such the Pb isotope ratios of exported Australian lead ores are generally low, typically with  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios  $< 16.5$  (Sangster et al. 2000), making this lead easily distinguishable from European lead, for example that used in seventeenth century Dutch paintings (Fabian and Fortunato 2010; Fortunato et al. 2005; Keisch and Callahan 1976; Sangster et al. 2000; van Loon et al. 2019). These major changes in long-term lead trade mean that lead whites produced and used as pigment in different centuries are liable to have significantly different Pb isotope ratios enabling recent renovation-retouching to be recognised.

### ***14.5.1 European Lead Production (Fifteenth to Seventeenth Century)***

In order to understand the lead isotope compositions of European paintings it is important to know the history of European lead mining. As most studies of lead white have focused on the sixteenth to seventeenth century, we will summarise which regions were active lead producers in this period, and how lead was used and traded. The two most important regions for lead production were Derbyshire in central England and the Harz region of Germany (Fabian and Fortunato 2010; Fortunato et al. 2005; Keisch and Callahan 1976). The lead mining history of these two regions is well known in the period between 1400 and 1600 because lead was key to silver production (Blanchard 1995). During this period, European silver was obtained using the Saigerprozess, which allows silver extraction from argentiferous copper by using large quantities of lead. Between 1450 and 1560, European lead production increased from 250 tons per year to 2250 tons, with a peak around 1530 with an annual production of 4200 tons (Blanchard 1995). At the peak of the silver production in the 1530s it was estimated that around two-thirds of lead in Europe was used to treat argentiferous copper with between 0.4 and 0.55 tons of lead used to process each ton of copper (Blanchard 1995).

The use of the Saigerprozess, together with fluctuation of the silver price during the sixteenth century, caused the lead mining industry to adapt multiple times and Derbyshire, Harz and Poland alternated as the main lead production centres (Blanchard 1995; Burt 1995). Lead production was affected by a series of technical and socio-political developments that had a major influence on trade in the middle of the sixteenth century. First, as a result of the earlier dissolution of the monasteries, priories, convents and friaries in the UK, there was an over-supply of cheap lead recycled from buildings that flooded the market and caused a drop in the lead price (from 1545 until 1549 (Burt 1995)). Second, a new silver extraction technique was developed around 1560. Mercury rather than Pb was used for silver extraction in a



process known as amalgamation. This change in the silver recovery process resulted in a drop in the demand for lead in a market that was already over supplied. In addition, the development of a new furnace smelting technique in the Mendip Hills in the UK allowed the waste (slag) of previous lead production to be reprocessed, again resulting in an increase in lead supply. This process was exported to the main lead production region of Derbyshire in the middle of the 1500s (Burt 1995).

These factors allowed England to become the main lead production centre from the end of the sixteenth century onwards, with the Derbyshire the focal point. The rise in the British mining industry contrasted with the fortunes of the generally deep mines in Germany and Poland. British lead deposits were relatively shallow while German and Polish mine were deep and required expensive technologies and a specialised workforce. Moreover, British lead mines were almost exempt from taxation in contrast to the high government taxes applied in Germany and Poland. The dramatic decrease of the lead price in the mid 1500s made the continental lead mine industry uncompetitive (Blanchard 1995, Burt 1995). This series of events resulted in an increase in British lead export from 450 tons in 1540 to 12300 tons in 1630 making the U.K. the major producer of Pb and its dominance continued for most of the seventeenth century.

## 14.6 Lead Isotope Analysis

One of the main issues in lead isotope analyses of lead white is obtaining samples as sampling paintings, especially when they are considered a masterpiece, is a delicate task, both physically and politically. Generally, the samples are kept to a minimum in both number and size, and restricted to areas of the paintings such as the border or areas of existing damage (Fortunato et al. 2005). Painting samples generally are taken manually by trained conservators using a scalpel under a magnification lens or with the help of stereo microscope. The small samples taken in this way can vary between hundreds of ng to  $\mu\text{g}$  in weight. This way of sampling, however, has some intrinsic problems:

- Unknown and variable amounts of contamination are included due to the sampling in different institutions/museums.
- Different operators perform the sampling leading to substantial differences in the way the samples are taken.
- Manual sampling causes variable amounts of sample to be taken such that sample size can differ by many orders of magnitude in weight, and it is not always possible to know how much painting matrix is contained in the samples.

These problems are not usually critical for the final analytical results, as lead white samples contain enough lead that contamination is irrelevant. Moreover the samples are treated and chemically purified before analysis to remove surface varnish layers that contain most of any environmental pollution. In some cases, however, the amount of lead white in the samples is low and possible contaminations,

either coming from the painting matrix that is not lead white or the surface, can produce unrepresentative data. This scenario is a problem because, in most of the cases, the samples are unique and no replicates are available. Importantly, however, quality control can be checked by monitoring the amount of lead in the samples so that, despite their unique nature, samples with little lead white can be discarded. These problems have the effect of reducing the available lead isotope data.

The issue of precise sampling was addressed by D'Imporzano et al. (2020a). The authors develop a micro-scalpel method to precisely sample lead white directly from cross sections of paintings. This method was designed to standardise the sampling procedure, reduce blank contamination, and minimise the amount of material obtained from a painting, and to store the sample material unused for isotopic analyses for further study. The possibility to store the painting material in cross-sections that can be re-utilised after lead isotope analysis, makes curators more willing to allow multiple sampling from a single painting and hence replicate analyses. Importantly, sampling from an existing cross-section negates the need to remove new material from a painting. If new samples are required, these can be taken as scrapings, embedded, sampled and then stored for future study. The developed tool can easily be transported. Moreover cross-sections can be shipped temporally to the laboratory and the sampling performed in a clean laboratory reducing any effect of blank contamination.

The improvement in the sampling method to expand available samples is crucial for lead isotope analyses, because data interpretation is heavily dependent on the database of lead isotope ratios of lead white of paintings. Increasing the number of analysed well-characterised paintings is necessary for the correct interpretation of lead isotope ratios of lead white from new and unknown paintings. Portable laser ablation techniques that use pulsed lasers may offer a potential solution for the future sampling of lead white to reduce the damage to painting/cross section and improve the precision of sampling (Knaf et al. 2017). The hope is that developing new, less invasive sampling methods will encourage institutions to allow more extensive sampling of paintings for lead isotope analysis.

There are two main techniques used for the analyses of lead isotope ratios: Thermal Ionisation Mass Spectrometry (TIMS) and Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS). In the last decades, MC-ICPMS instruments have been used regularly to characterise lead isotope ratios of lead white. The reason of the preference of this technique over the TIMS is due to:

- MC-ICPMS can analyse samples directly in solution, reducing greatly the time of sample preparation.
- The data acquisition is faster and more automated compared to TIMS, meaning that sample throughput is more efficient.
- Instrumental fractionation between the different Pb isotopes (mass fractionation) cannot be directly monitored using TIMS and the long term accuracy is assessed by measuring a series of standards (see below). This issue can be overcome using an artificially enriched double Pb isotope “spike” but that requires multiple analysis and the use of expensive spikes.

- For samples containing between 50 and 100 ng of lead the MC-ICPMS provides the same accuracy and precision as the double spiked TIMS technique (D’imporzano et al. 2020a).

Typical samples of lead white contain several hundreds of ng of lead such that sample dilution is required. Hence, the MC-ICPMS is the best option for lead isotope analyses of lead white. The use of TIMS, that have a higher precision and accuracy for smaller ion beam, is required when the samples contain smaller amounts of lead (< 10 ng). The recent development of  $10^{13}$  Ohm resistor amplifiers, however, allows MC-ICPMS measurement of 5 ng of lead while maintaining similar accuracy and precision compared to 75 ng Pb sample using normal amplifier (Klaver et al. 2015; Koornneef et al. 2014, 2019). If such small samples are analysed, however, it becomes important to precisely monitor the blank contamination.

The general procedure to prepare the sample is based on the dissolution of the lead white in nitric acid. Subsequent sample preparation can vary slightly from laboratory to laboratory. After dissolution, the sample is treated with chromatography in order to obtain a pure lead fraction (D’imporzano et al. 2020a). Other works argued that for samples containing only pure lead white, chromatographic purification with chromatography can be avoided provided that Ca content is not below 200 ppm (Fortunato et al. 2005).

Avoiding any matrix interference is, however, important because isotope analyses on an MC-ICPMS are subject to large instrumental mass fractionation that can be influenced by even small (ppm) levels of other elements, and chromatographic separation to ensure the highest quality data is highly recommended. Details of how corrections are applied to account for mass fractionation and more information on isotope analysis, MC-ICPMS theory and mass-bias can be found in (Albarède and Beard 2004) and only briefly summarised below.

Lead has only one stable isotope,  $^{204}\text{Pb}$ , and therefore internal sample correction for mass bias fractionation produced in the mass spectrometer is impossible, as at least two stable isotopes are required. Correction for instrumental fractionation is typically performed by analyses of reference materials (usually pure Pb solution in 1%  $\text{HNO}_3$ ) with known isotopic composition in between analyses of unknown samples (so-called standard sample bracketing—SSB). The advantage over the TIMS method is that switching between sample and standard can be performed within a few minutes. The known isotopic composition of the reference material is used to calculate, following an exponential law, the instrumental mass fractionation factor that is then used to correct the samples data. This approach, however, cannot correct for differences in instrumental mass fractionation between the sample and reference material caused by variations in the sample matrix, therefore requiring a chromatographic purification step to assure the best accuracy possible of the analysis.

An alternative method is to use the Double Spike (DS) technique. DS allows for internal correction of the instrumental mass fractionation, and the use of a standard solution between samples is unnecessary. The accuracy of the DS is independent of the matrix composition of the sample, and the purification of the lead of the sample is less important in this case. The intense use of the DS, however, can cause memory

effects in the instrument making this technique unsuitable for routine analysis (D'Imporzano et al. 2020b) and it is expensive and more time consuming.

## 14.7 Current State-of-the-Art

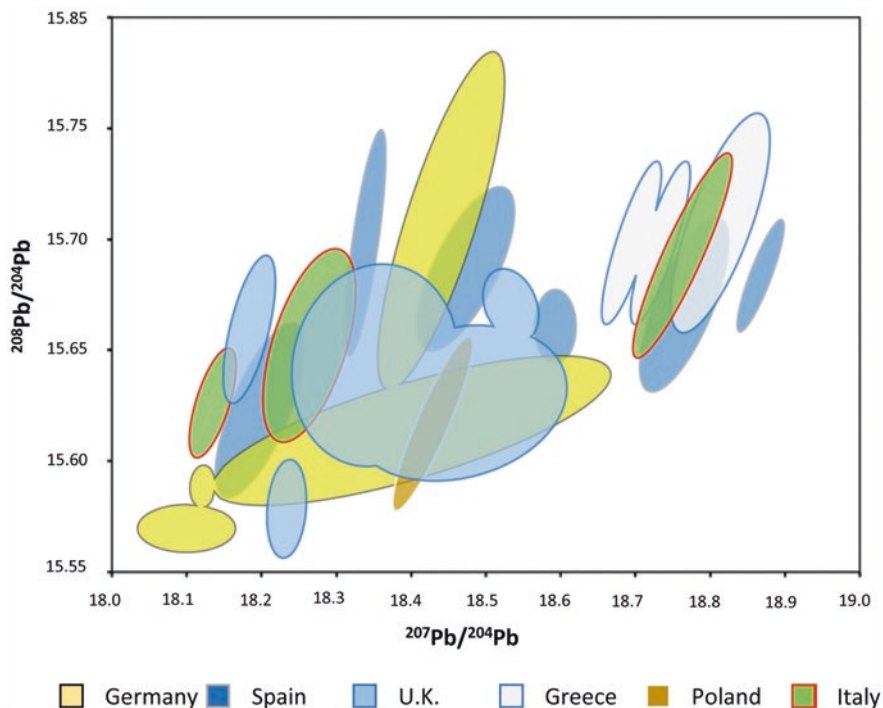
### 14.7.1 *Lead Isotope Ratios in Paintings: Provenance and Identification*

Lead isotope analyses of lead white in paintings have provided information about: (i) pigment provenance; (ii) artistic periods which can lead to; (iii) distinction between modern and historical lead white; iv) valuable information for attribution of paintings.

Place of origin, provenance, of lead in the lead white of a painting can only be determined by direct comparison to data obtained from lead ore deposits. Ideally isotopic analysis of ore minerals should be confined to lead deposits that were active at the time of creation of the artwork. In that case, the isotopic data can be used to provide useful insights into the trading history of past societies. This has been successfully applied for archaeological artefacts (Pollard and Heron 2008; Stos-Gale and Gale 2009). The vast majority of the archaeological studies using lead isotope ratios, however, are focused to reveal the trade in metals in the Mediterranean in the bronze age (Pollard and Heron 2008) and it is these data that currently form the majority of the Pb isotope database used for provenance studies.

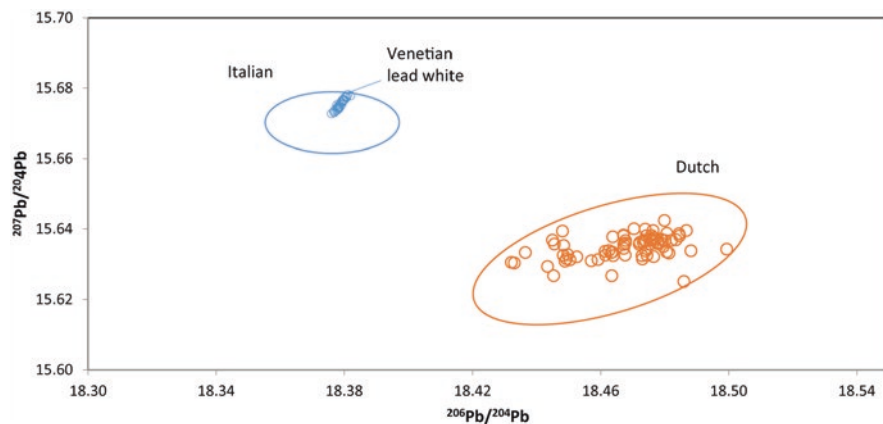
When all the isotopic data from individual regions are combined, the result is a graph with overlapping Pb isotope ratios. As an example, lead isotope data from European ore deposits are summarised in Fig. 14.1. A key aspect to the data interpretation is knowledge of which mines were active at the relevant time.

Figure 14.1 demonstrates that the Pb isotope ratios from lead white present in seventeenth century Dutch/Flemish paintings fall in an area characteristic of three different countries. These represent mines in Poland, England and Germany, specifically Harz Mountains, Germany, Nidderdale, Derbyshire in the UK. Fortunato et al. 2005, concluded it is impossible to identify provenance based on lead isotope ratios alone. If the information about the mining industry in Europe during the seventeenth century are taken in account, however, it is most likely that the lead has a British origin, probably Derbyshire, as this region was the most active for the production of lead in the seventeenth century (Blanchard 1995; Burt 1995). This discussion emphasises the need to know the lead production history in order to interpret the isotopic data. Importantly, however, there are also some clear regional variations in the Pb isotope compositions of mining districts. Fabian and Fortunato 2010 pointed out the distinction between seventeenth century Dutch paintings and sixteenth to seventeenth century Italian paintings (Fig. 14.2). The Pb isotope data show two well resolved clusters, consistent with the different geological environments of the lead mines in the Alps and northern Europe.



**Fig. 14.1** Lead isotope ratio figure showing the  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios for lead deposit in Europe. The data are taken from the literature (e.g. (Fortunato et al. 2005) and Oxford lead isotope database OXALID). The red circle indicates the range of seventeenth century Dutch/Flemish paintings. (Fortunato et al. 2005)

The marked isotopic difference between Italian and Dutch lead white is particularly useful due to the many study-visits made by Dutch painters to Italy. The Pb isotope differences make it possible to recognise if a painting was made by a painter while studying abroad because it is unlikely that painters would have transported bulky and dense pigments with them, especially when lead white was readily available in Italy. The painting by Willem Drost, presented in the study of D’Imporzano et al. (D’Imporzano et al. 2020a) provides an interesting case study. The artist was active in Amsterdam (1652–1654) before he travelled and died in Venice in 1659. The painting entitled, *Roman Charity* (SK-C-1802) was thought to derive from his Italian period (1655–1659) due to strong Italian stylistic influences. The lead isotope ratios of the painting are, however, consistent with seventeenth Century Dutch lead white, in particular in the years around 1650 (star in Fig. 14.2). In this period the artist was known to be active in Amsterdam either in Rembrandt’s studio or in his own. The isotopic data are within analytical error of samples from Rembrandt’s workshop painting “Holy Family” (SK-A-4119), which was painted in the period 1642–1648. Italian influences in the painting can be explained by the numerous Italian works that were in Amsterdam at the time. Further support for a Dutch



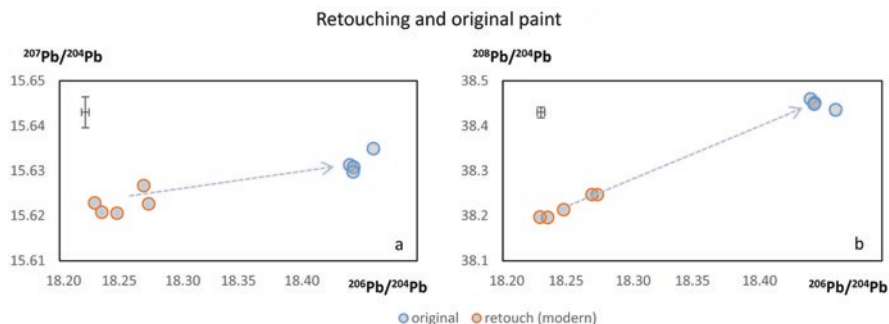
**Fig. 14.2** Lead isotope ratio figure showing a comparison between seventeenth century Dutch paintings and sixteenth to seventeenth century Italian paintings (Fabian and Fortunato 2010; Fortunato et al. 2005; D'Imporzano et al. 2020a). The Italian group is characterised by samples analysed by (Fabian and Fortunato 2010), light blue ellipse, while the blue dots are from lead white cones representing pure Venetian lead white found in a shipwreck (D'Imporzano et al. 2020). The star represents an analysis of a painting from Drost, see text for details

provenance comes from the fact that Drost made a preparatory drawing for the painting that dates from his Amsterdam period. Integrating this information with the lead isotope data, it is considered highly probable that the painting was produced by the artist in Amsterdam before his departure to Rome in 1655 (D'Imporzano et al. 2021).

Currently available Pb isotope data from well characterised paintings from other regions and periods are limited, primarily due to the difficulty in obtaining samples for destructive analysis. Unfortunately this means that Spanish, German, British and French paintings cannot be easily characterised. The database for lead isotope ratios of lead white will be expanded further in the future in order to have more information on these paintings.

### 14.7.2 Post Production Retouching and Modification

Lead isotope ratios of lead white can help identify retouching made to paintings significantly post production. Equally if a painting has been restored several decades or centuries after its initial production, it is almost inevitable that lead isotope analysis will resolve the different generations of lead white. In their pioneering work, Keisch and Callahan 1976 analysed 429 paintings produced between the thirteenth to the twentieth century and demonstrated that lead isotope compositions of lead white changed over time. In particular, the data show that lead isotope ratios of lead white are markedly more variable after the eighteenth century ( $> \times 10$ ).



**Fig. 14.3** Pb isotope ratio diagram contrasting original and retouched paint sampled for a painting from De Gelder (D’Imporzano et al. 2020a). The cross indicates the long term reproducibility of the instrument (analytical error) after D’Imporzano et al. 2020b

The increase in variability of lead isotope ratios of lead white was also reported in two other papers Fortunato et al. 2005 and D’Imporzano et al. 2020a. Fortunato et al. 2005, compare data from Flemish and Dutch paintings with samples of “modern lead white”. Figure 14.3 demonstrates that the Flemish/Dutch paintings form a distinct cluster compared to modern lead white (D’Imporzano et al. 2020a). The study from Fortunato et al. 2005 reports that a specific sample taken from a Rembrandt painting (sample G26-G, painting *Minerva in her study*, Mauritshuis, NL) falls among the region of modern lead white. The sample is from an area of the painting that was restored most probably at the end of the eighteenth century. Similarly, D’Imporzano et al. 2020a, found that 5 samples, taken from retouched part of a painting from De Gelder, have isotopic compositions that are consistent with modern lead white (Fig. 14.3).

In all these cases, lead isotope ratios were able to distinguish different generations of lead white used on an individual painting. In this context, it is notable that the variability in lead isotope ratios of lead white increased markedly after the eighteenth century. This change happened in a period when the world was going through unprecedented socio-economical change, with the advent of the industrial revolution and the establishment extensive extra-European lead production. These observed long-term temporal changes can be used in order to identify retouching and paintings made before or after a certain period, and could be a powerful tool to identify forgeries.

### 14.7.3 *From Macro to Micro: Lead Isotope Ratios Within a Painting*

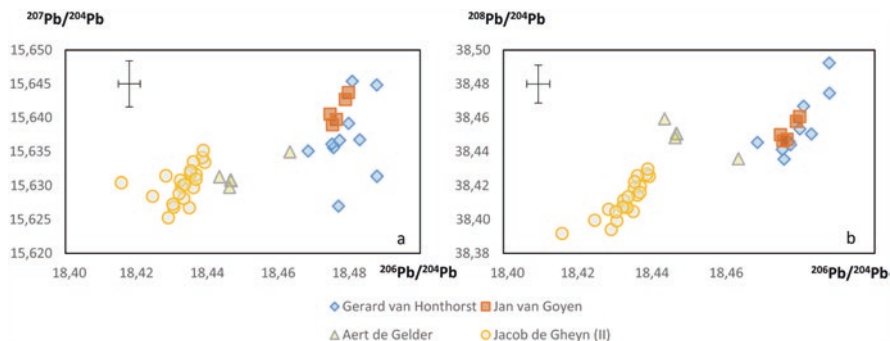
As outlined above, lead isotope data can distinguish different artistic periods/geographical regions. One important parameter that has not been fully assessed is how well lead isotope analyses can distinguish two paintings produced in the same

period/region. This information will be crucial in studies of authentication or when an unknown painting requires attribution. In order to answer this question it is crucial to know the range of lead isotope heterogeneity present within a certain artistic cluster and the heterogeneity of lead isotope ratios of the lead white within an individual painting. This question arises because authentication studies are generally made based on the analyses of a limited number of samples and compared against a small database or just one or two other samples from a comparison painting. The case of the *Saint Praxedis* (1655, Private Collection) provides a good example as the attribution of the painting is highly debated with some arguing that it represents an early Vermeer while others suggest it to be an Italian copy after Felice Ficherelli's *Saint Praxedis* (Wheelock 1986). Prior to auction in 2014, the *Saint Praxedis* was subjected to Pb isotope analysis. Lead isotope data were determined from two samples of the *Saint Praxedis* and then directly compared with a sample from Vermeer's *Diana and her Nymphs* (1653–4, Mauritshuis, The Hague, inv. n. 406). The Pb isotope data of the two paintings were analytically 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 Pb isotope ratios. Based on the current state of knowledge, however, this assumption was not proven. Lead isotope data available at that time establish that paintings produced in the same region and time have limited lead isotope variation. A conclusion that the *Saint Praxedis* was not produced in Italy but in the Netherlands is therefore supported. There was, however, insufficient information about the Pb isotope variation within individual paintings or within the oeuvre of individual artists from the Netherlands to make a direct attribution. Equally it was unknown if or how Pb isotope ratios of lead white change during the seventeenth century and across the continent.

As the heterogeneity of lead isotope ratios within an individual painting is unknown, this makes the direct comparison of individual samples from a limited number of different paintings by the same artist difficult to interpret. To address these questions a study on the heterogeneity within individual paintings was conducted by analysing five paintings from the Rijksmuseum Amsterdam (D'Imporzano et al. 2020a). The study focused on paintings created during the seventeenth century in the Netherlands. The paintings were sampled multiple times, with a minimum of five samples taken from different locations from each painting. The study also investigated the potential isotopic differences in lead between different paint layers, including the ground.

The study found that while all the samples have isotopic values in line with those previously reported for seventeenth century Dutch/Flemish paintings, four out of five paintings have lead isotope ratios that vary more than analytical error (Fig. 14.4). The isotopic heterogeneity found in the paintings corresponds to several times the long term reproducibility of the analytical method on each of the reported lead isotope ratios. In particular, the highest variation was found for the case of the painting of de Gheyn II where data show that the heterogeneity was 7.6 times the long term reproducibility for  $^{206}\text{Pb}/^{204}\text{Pb}$ , 2.6 for  $^{207}\text{Pb}/^{204}\text{Pb}$  and 3.4 for  $^{208}\text{Pb}/^{204}\text{Pb}$ . The





**Fig. 14.4** Lead isotope distribution from four Dutch artists. The data show the lead isotope ratios distribution obtained by analyses of several samples coming from 5 different paintings (two paintings for van Honthorst made in the same period were analysed and are reported using the same symbol). The cross indicates the long term reproducibility of the instrument (analytical error) after reference (D'Imporzano et al. 2020a)

variation of lead isotope ratios of lead white in this painting, especially on the ratio  $^{206}\text{Pb}/^{204}\text{Pb}$  was controlled by two samples taken from the ground layer. If these samples were ignored, the Pb isotope heterogeneity still remains outside analytical error, up to 4 times (D'Imporzano et al. 2020a).

The study investigated the reason for the isotopic heterogeneity in individual paintings and included analyses of a large number of samples of contemporary (sixteenth century) commercially produced pure lead white. Lead white was sampled from cones of pure pigment recovered from a ship wreck that was trading goods from Venice to Constantinople (Batur 2019) and sunk in the Mediterranean sea. The lead white was studied because it was produced around 1580, as the ship sunk in 1583 and can give insight on lead white produced at that time. In this way, it was possible to analyse historical lead white that was untouched for centuries and that retains the original lead isotope composition of its production. Although the lead white was under water for hundreds of years, it was unaffected by alteration due to the high content of lead in lead white and the low concentration of lead in seawater and the pristine preservation of all but the outside of the lead white cone. The Pb isotope data of multiple lead white cones are within analytical error and demonstrate that the product was homogeneous when shipped. This conclusion should not come as a surprise because the lead white production method involves steps of melting metallic lead, washing and grinding of huge quantities of lead white that will produce homogenisation (Stols-Witlox 2014). The study used Venetian lead white but the similarity of the general production methods across Europe (Stols-Witlox 2014) implies all commercially produced batches of lead white would be homogeneous. The heterogeneity recorded by the individual paintings analysed in D'Imporzano et al. 2020b imply either mixing of different batches of lead white or the mixing of lead white with other lead bearing material in the matrix of the painting that had different lead isotope compositions. This heterogeneity can have two explanations:

The first hypothesis would imply that the lead white used for paintings come from different batches having different isotopic values. It is possible that different lead white batches contain different lead isotope ratios if different starting lead was used. Based on trading records, however, the sources of lead appear to be stable for extended periods (several years), which would argue against significant short term isotopic variations, a point explored in more detail in Sect. 14.7.3.

The second hypothesis to consider is that the production of a painting involves the combination of many different lead bearing materials. In particular, many recipes advise to use of oils that have been processed by a variety of methods. Recipes for preparatory layers mention boiled oil, fat oil and drying oil (Stols-Witlox 2014). These preparations aim to improve the drying rate (polymerisation) of the oil. Usually lead based compounds were used as a siccative agents, as written in a recipe for fat oil treatment with siccatives. Stols-Witlox et al. 2014 list multiple recipes for oil preparation using lead as siccative agent: De Mayerne's recipe for siccative oil written between 1620 and 1646 suggests to treat the oil with water and PbO (PbO/oil/water ratio of 1/4/4 (w%)) (Mayerne 1620–1646). King (1653–7) provides a recipe for a fat oil that is prepared by placing linseed oil in the sun for three weeks after the oil had been mixed with lead white, minium, sawdust and crumbs of brown bread (Stols-Witlox 2014). Stalker and Parker (1688) advised to place linseed oil in the sun in a lead glazed vessel. Dutens (1779) describes how fat oil is made by slowly heating litharge (lead II oxide) and lead white with linseed oil. In a later edition, Dutens (1803) gives a recipe for a 'fat or drying oil' that is prepared by exposing linseed oil with lead white and litharge to the sun for eight days, stirring it once or twice per day (Stols-Witlox 2014). The use of siccatives, metal salts such as those containing lead, manganese or zinc, which act as a catalyst for the polymerisation of the oil binder, not only appear in recipes for the preparation of oil binders advised for use in preparatory layers, but also appear as additions during the ground preparation itself, e.g. for earth or clay-bound layers, addition of small amounts of lead white or minium are suggested (Stols-Witlox 2014).

The combination and mixing of these lead-based compounds in different layers of the painting could cause a variation of lead isotope ratios within and between paintings according to the amount of lead sources mixed in the process. In order to cause a significant isotopic change, however, the lead composing the PbO should come from a different source, which as explained below would imply lead sources produced at different times.

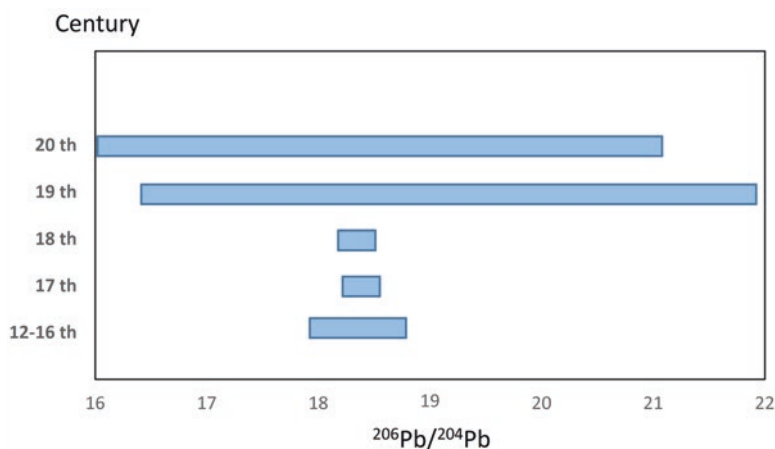
#### ***14.7.4 Temporal Change in Lead Isotope Ratios of Lead White: A Case of Study for Seventeenth Century Dutch Paintings***

The first documented variation in lead isotope ratios of lead white with time was documented by Keisch and Callahan (Keisch and Callahan 1976). The study found that after the nineteenth century lead isotope ratios of lead white are more variable.

The Pb isotope composition of lead white undergoes significant change and becomes more variable after the industrial revolution in the mid-eighteenth century (Fig. 14.5), and remains highly variable during the nineteenth and twentieth century. This change in isotopic composition of the pigment is due to a combination of the opening of many extra-European lead mines, changes in the lead trading and the opening of new centres of lead white production.

The variation of lead isotope ratios of lead white in paintings made after the eighteenth century have not been studied systematically, however, a detailed investigation has been made for seventeenth century Dutch paintings (D'Imporzano et al. 2021). Analyses of this artistic group (Fabian and Fortunato 2010; Fortunato et al. 2005; Wheelock 1986) indicate that the lead isotope compositions of lead white from seventeenth century Dutch paintings forms a cluster but also record significant Pb isotope variation equivalent, to 44.5 times the analytical error for  $^{206}\text{Pb}/^{204}\text{Pb}$ . D'Imporzano et al. 2021 evaluate the processes that control the observed variation in seventeenth century Dutch paintings. Based on the analysis of 77 painting from 27 Netherlandish painters, the study examined if the isotopic variation reflected artistic groups or the time of production. Lead white samples were taken from authenticated paintings from the collections of the Rijksmuseum and Mauritshuis. In all cases, the date of production was known with an uncertainty of a maximum  $\pm 2.5$  years. These data, reproduced in Fig. 14.6, demonstrated that by using lead isotope ratios alone, it was impossible to achieve a clear distinction between paintings produced within the oeuvre or workshop of an individual artist (D'Imporzano et al. 2021).

The lead isotope ratios of most terrestrial sources define general co-linearity because the isotopic ratios are controlled by geological age and U/Pb and Th/Pb ratios. This is because U and Th generally have similar geochemical behaviour. The  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio records the largest variation and is the best ratio to identify patterns



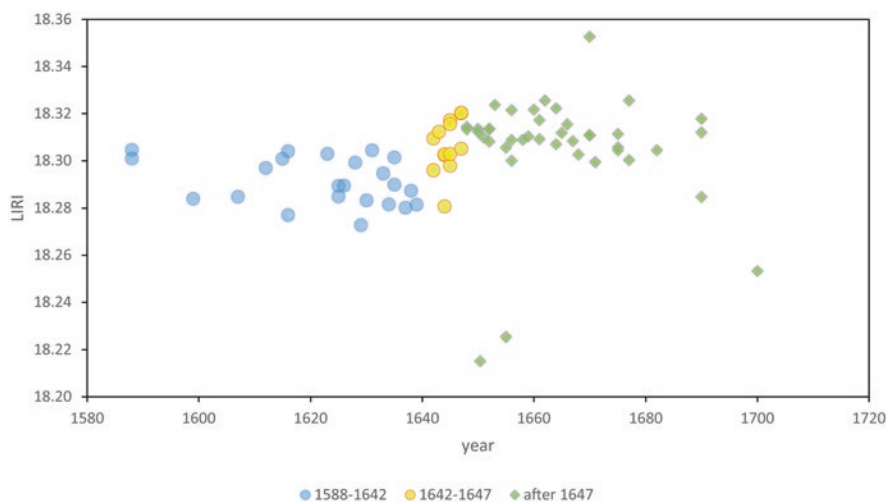
**Fig. 14.5** Temporal variation in lead isotope ratios in lead white reported by Keisch & Callahan (1976)

of lead isotope variation in lead white. Using a single Pb isotope ratio, however, fails to fully utilise all the Pb isotope variation,  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$ ,  $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$ . In order to better visualise all aspects of the Pb isotope data, Keisch and Callahan 1976 [1] developed the Lead Isotope Ratio Index (LIRI). The method applies a correction to the  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio based on  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  values following the empirical equation:

$$\begin{aligned} \text{LIRI} = & 35.385 + 0.4729 * \left( ^{206}\text{Pb} / ^{204}\text{Pb} \right) \\ & - 0.5519 * \left( ^{206}\text{Pb} / ^{204}\text{Pb} \right) * \left( ^{207}\text{Pb} / ^{206}\text{Pb} \right) \\ & - 8.2561 * \left( ^{208}\text{Pb} / ^{206}\text{Pb} \right) \end{aligned}$$

The LIRI index gives an indication of whether a sample lies within a specific cluster of isotopic ratios and allows the integrated isotopic data to be easily plotted against time, Fig. 14.6. Using the LIRI to visualise the isotopic data, using information from all the relevant Pb isotope ratios. However, if direct comparison of two samples is required, it is important to analyse the data using the original lead isotope ratios because identical LIRI values can be obtained from different raw data and therefore using only the LIRI could lead to false interpretation (Keisch and Callahan 1976). This method of data analysis is, however, useful when lead white samples come from an artistic group.

The data reported in Fig. 14.6 establish that the paintings produced in the Netherlands between 1588 and 1642 have LIRI values between 18.271 and 18.304 (D'Imporzano et al. 2021). The 5 years following 1642 show a transition to higher LIRI values that reach an “equilibrium” in the period 1647–1680. In these three



**Fig. 14.6** Lead Isotope Ratio Index (LIRI) against time. The graph shows the data for lead white samples from 77 different Dutch paintings plotted against time (D'Imporzano et al. 2021)

decades LIRI values are between of 18.297 and 18.326. Samples from paintings made after 1680 appear to be more variable but the dataset from this period is limited, as is the coverage of paintings from the start of the seventeenth century. Despite these limitations, the study appears able to distinguish paintings from the seventeenth century Dutch period, based on their time of production. The explanation for variation in the lead isotope ratios of lead white appears related to changes in the socio-political and economic factors that controlled the lead trade in the seventeenth century. The major change in Pb isotope compositions between 1642 and 1647 is coincident with the English civil war. England was the main producer of lead before that period, and most lead white in north Europe was probably made using English lead. Changes in the supply chain during the English civil war led to changes in lead supply. The limited data available for the end of the seventeenth century show that the LIRI is more variable, and it appears that the LIRI values start to lower to values comparable to the beginning of the century. The end of the seventeenth Century was a period of major tension between the Dutch Republic, England and France, with a series of wars starting in the 1670s until the end of the century. This period of social turbulence would undoubtedly have altered the Pb supply chain and therefore explains the variance of the lead isotope ratios found in lead white. More data are needed in order to clarify this hypothesis and determine the exact changes in the source of Pb to the Netherlands. At the actual state of the art, the time-dependant variation of the lead isotope ratios of lead white is able to distinguish lead white used between 1588 and 1642 and between 1647 and 1680. This can be used in order to distinguish the work of artist active in different decades, in particular if they were active before and after the transition recorded in the period 1642–1647. In this optic lead isotope analysis could also help to distinguish the early and late work of an artist active in the middle decades of the century. The study of D'Imporzano et al. [2021](#) represents a first step to obtaining a better understanding a detailed record of the temporal changes in Pb isotope ratios in lead white over time but additional studies are required from other European countries to examine the extent that Pb trade was local or regional.

## 14.8 Lead Isotope Tool Box for Identification

The previous sections discussed how lead isotope ratios of lead white have been used in order to study paintings, and how information about provenance, affiliation to artistic groups and variance of lead isotope ratios within painting or artistic group can be used in cultural heritage studies. The majority of the information obtained to date, however, is relevant for the seventeenth century Dutch paintings. This section will provide guidelines of how to use lead isotope analyses on paintings that derive from artistic groups that have not yet been studied. The methodology is designed to help attribute the artist or discover forgeries.

In a case that a painting is analysed for lead isotope ratios, and the artist is unclear the following approach can be used. The first step is to gather as much background

information as possible. Information about date of production, artist name or artistic affiliation and region of provenance all can contribute greatly to interpretation of lead isotope data. As explained previously, the sampling strategy is fundamental for the correct characterisation of lead isotope ratios. Consequently, the study of a painting should be based on the analysis of multiple samples and these samples should be taken from areas of the painting containing lead white as pure as possible, in order to limit any unwanted external contamination. Ideally, 3–5 samples would be sufficient in order to assess correctly the variability of lead isotope ratios within the painting.

If the painting does not belong to a period of which the lead isotope composition is known (sixteenth to seventeenth century Dutch or Italian), then lead isotope data interpretation requires the analyses of samples from paintings produced at the same time and in the same region. Based on the current state-of-the-art, however, it is not essential (but recommended when possible) to have paintings from the same artist, especially if not painted in the same period. These requirements may prove difficult, as obtaining sample material from well-characterised paintings (painter and time) is usually difficult and time consuming. Comparison of lead white samples of known provenance, i.e. which artistic period and region, is fundamental for correct attribution. If these steps are followed then lead isotope analyses can be used to help identify the artist.

As an example, we use the uncertain origin of a Spanish paintings purported to be from the seventeenth century. Currently there are extremely limited data from Spanish paintings and a lead isotope database for these painting, dated between the 1600 and 1750, does not exist. The information obtained from the analysis of a single sample would be therefore limited. In the absence of a comparison database, only three data interpretation outcomes are possible: (i) the lead white is consistent with one of the artistic groups characterised so far (Dutch, Italian); (ii) the lead white has isotopic ratios that fall in an area where modern lead white is found; (iii) the lead white has values inconsistent with previously analysed paintings. Option one would imply that the artist, if Spanish, used a foreign lead white or that the painting is not Spanish. The second option would suggest that the painting is a modern copy, or that seventeenth century Spanish lead white has a similar isotopic distribution to modern lead white. The third option does not allow attribution of the artist. In all these scenarios, the lead isotope analyses provide little concrete information. If, however, samples from other Spanish paintings of the same period were analysed, then it would be possible to have a control group to compare the data with, and lead isotope analysis would provide a clear indication for attribution. Without following the proposed approach the identification of many paintings using lead isotope analysis would be impossible, or worse, could give incorrect information. Currently, it is only possible to use lead isotope analysis to identify or discover forgeries of Dutch and Italian paintings in respectively the sixteenth and seventeenth centuries.

## 14.9 Conclusion

The study of lead isotope ratios of lead white demonstrates that it is possible to identify the provenance of the Pb used in the pigment and the difference in lead provenance can identify pigment originating from different regions. In this way, it is possible to use lead isotope ratios to identify Italian and Flemish/Dutch paintings produced in the sixteenth to seventeenth century. Lead isotope variation in lead white increases in modern time, and it is possible to identify an increase in lead isotope variation starting after the mid-eighteenth century, when extra-European lead deposits started to dominate the lead trade.

The lead isotope analysis of paintings in recent years focused on the identification of isotopic variance at different levels in order to provide a more quantitative interpretation of the data. Variance has been identified at three different levels: within a painting, within an artistic group and relative to time, most notably in seventeenth century Dutch paintings. The variation of lead isotope ratios found within a single painting and in seventeenth century Dutch paintings suggests that future studies employ a multi-sampling method for lead isotope analyses of lead white, especially when an analysis is applied for authentication. The heterogeneity found within individual paintings implies that the comparison of single samples of lead white between two paintings may provide insufficient information to make attribution to a region or an artist.

Available data suggest that it is possible to identify different artistic groups within a specific time and region using lead isotope analysis. Within these groups, however, it is impossible to distinguish different artists, especially if active at the same time, using lead isotope data alone. The detailed study of the seventeenth century Dutch period, however, establishes that lead isotope ratios of lead white follow a time-dependant trend. This variation is best illustrated using LIRI and indicates that it is possible to assign a Dutch painting to a certain part of the century, and potentially distinguish artists active in different decades, or can help to distinguish between the young or old work of the artists. This information represents a powerful tool to help in authentication of seventeenth century Dutch paintings.

For the study of paintings coming from other periods and regions, lead isotope analysis can still be a powerful tool if guidelines listed in Sect. 14.9 are followed. This review suggests that lead isotope analysis of lead white will become a powerful tool in the field of cultural heritage. The information obtained via this method cannot be obtained with other techniques and the isotopic composition can give insight on the material used that can allow distinction of original and modern paintings and as the database is expanded, a far greater understanding of lead trading will be established and how this was influenced by socio-political events in Europe and beyond.

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