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Contribution of geochemistry and geochronology to the knowledge of the history of the uses of modern musical instruments

Marie-Gabrielle Durier

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Contribution of geochemistry and geochronology to the knowledge of the history of the uses of modern musical instruments

Apport de la géochimie et de la géochronologie à la connaissance de l'histoire des usages des instruments de musique

Thèse de doctorat de l'université Paris-Saclay

École doctorale n°129, Sciences de l'Environnement d'Ile-de-France (SEIF)
Spécialité de doctorat : Physico-chimie de l'atmosphère
Graduate School : Géosciences, climat, environnement et planètes. Référent : Université de Versailles Saint-Quentin en Yvelines (UVSQ)

Thèse préparée dans les unités de recherche **LSCE (Université Paris-Saclay, CNRS, CEA, UVSQ) et CRC (UAR3224, CNRS)**, sous la direction de **Christine HATTÉ**, directrice de recherche CNRS/CEA/UVSQ, le co-encadrement de **Stéphane VAIEDELICH**, responsable du laboratoire du musée de la musique de Paris, équipe ECR, CRC

Thèse soutenue à Paris, le 9 mai 2022, par

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Titre : Apport de la géochimie et de la géochronologie à la connaissance de l'histoire des usages des instruments de musique modernes.

Mots clés : Géochimie, Géochronologie ^{14}C , Instruments de musique, Période moderne, Objets patrimoniaux

Résumé : Deux techniques avancées couramment utilisées en archéométrie : la géochronologie ^{14}C (MICADAS) et la géochimie isotopique du strontium (MC-ICP-MS, Neptune) ont été explorées ici afin d'évaluer la faisabilité et les limites d'adaptation aux problématiques des collections muséales d'instruments de musique de la période moderne. Ce travail s'est concentré sur les vernis huile de lin/colophane ; le corpus d'étude a été étendu aux vernis de mobilier et hippomobiles du début du 18^e s. et comprend également des cordes de boyaux anciennes comme témoins matériels de l'histoire des usages. Le volet géochronologie ^{14}C (datation) a débouché sur le développement de protocoles d'échantillonnage et de traitements chimiques adaptés selon la nature des matériaux. Des éléments ont également permis d'approfondir la connaissance des objets patrimoniaux analysés et leurs usages (impact de restaurations, réemploi de matériaux, ingrédients, etc.).

Le volet isotopie du strontium (traceur d'origine géographique) a été testé sur des liants organiques du marché actuel. La conservation de la signature $^{87}\text{Sr}/^{86}\text{Sr}$ depuis le socle géologique jusqu'à la résine de pin et la colophane (après distillation) a été validée pour des échantillons sol/résine/colophane d'origine connue. Une sélection de colophanes a fourni des mesures $^{87}\text{Sr}/^{86}\text{Sr}$ cohérentes avec les cartes géochimiques. Cette étude d'état d'avancement méthodologique sur deux volets montre la possibilité de surmonter des écueils comme la taille de l'échantillon ou les niveaux de contamination. Elle a fait l'objet de trois publications (Durier et al. 2019, 2021, 2022) et ouvre des perspectives pour aborder les questions de la contrefaçon, la retouche, de l'entretien ou la restauration sur l'instrument de musique, et de la provenance des liants organiques utilisés dans les vernis en lutherie, étendus aux autres objets patrimoniaux.

Title : Contribution of geochemistry and geochronology to the knowledge of the history of the uses of modern musical instruments.

Keywords : Radiocarbon dating, Musical instruments, Modern period, Geochemistry, Heritage objects

Abstract : The PhD study presented here explores the feasibility and the limits of adapting two advanced techniques currently used in archaeometry: ^{14}C geochronology (MICADAS) and isotope geochemistry (MC-ICP-MS NEPTUNE), to the issues of the instrumentarium of the modern period kept in museum collections. The research focused on linseed oil/colophony varnishes; the material corpus was extended to varnishes of pieces of furniture and horse-drawn carriages mainly from the early 18th c. and also includes early gut strings as a testimony of the material history of uses. The ^{14}C geochronology study led to the development of sampling protocols and chemical treatments for analyzing materials according to their nature. The study also provided new insights to deepen our knowledge of the analyzed objects and their uses (impact of restorations, reuse of materials, ingredients, etc.).

The Sr isotope study (geographical provenance) was tested on organic binders from the current market. The conservation of the $^{87}\text{Sr}/^{86}\text{Sr}$ signature from the bedrocks to the pine resin and colophony (after distillation) was validated for a corpus of pine soil/resin/colophony with a known provenance. The selected colophony provided $^{87}\text{Sr}/^{86}\text{Sr}$ measurements consistent with geochemical maps. The state of advancement in the methodological adaptations for both approaches highlights the possibility of overcoming pitfalls such as the sample size or the contamination levels. Three articles were published (Durier et al. 2019, 2021, 2022). This research opens up new perspectives to address the issues of counterfeiting, retouching, maintenance or restoration on musical instruments, and on the provenance study of organic binders for varnishes used in violin making, extended to other heritage objects.

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Acronyms

CRC	Centre de Recherche sur la Conservation
CRCC	Centre de Recherche sur la Conservation des Collections
ECR	Équipe de Conservation et de Recherche, Musée de la musique, Paris
LRMH	Laboratoire de Recherche des Monuments Historiques
LSCE	Laboratoire des Sciences du Climat et de l'Environnement
KIK-IRPA	Koninklijk Instituut voor het Kunstpatrimonium - Institut Royal du Patrimoine Artistique
KMKG-MRAH	Koninklijke Musea voor Kunst en Geschiedenis – Musées Royaux d'Art et d'Histoire
RMAH	Royal Museums of Art and History
MNVT	Le Musée National de la Voiture et du Tourisme

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GENERAL INTRODUCTION

1. Introduction and research aims

1.1. General context

This PhD is part of a research strategy at the Musée de la musique in Paris to integrate archaeometrical approaches in order to enhance the way musical instruments from the modern period (from the 16th to 19th c.) are examined and documented. The Musée aims to describe the history of music through its collection and to assess the cultural values of each of the objects in the inventory. Researchers undertake continuous efforts to deepen scientific knowledge about instruments, for example, to date their appearance in the general chronology of music, to understand the chronology of their making, uses or restorations during their long material history, to develop historically informed reconstructions and musical practices, to better preserve and promote the collection, etc. These different fields including dating, origin studies, material characterization, restoration, conservation and valorisation are closely linked.

To examine musical instruments, it is necessary to combine a wide range of specialties due to their material complexity including restoration, conservation, organology, history, instrument making or material sciences. Additionally, new methods and technologies are steadily being added to the scientific techniques already available in museum institutions. These multidisciplinary and multi-technique approaches make it possible to collect data and to confront historical documentation with scientific analyses.

During this PhD, methodological adaptations were essential to add the advanced tools of ¹⁴C geochronology and strontium geochemistry to the panel of the other scientific analyses used in museum institutions (dendrochronology, museology, etc.). In fact, they are routinely used in archaeology and environmental sciences but seldom applied to the *instrumentarium* of the modern period. Currently, very few articles in the literature have reported the application of ¹⁴C dating on modern musical instruments including wooden parts, vanishes or gut strings (Chase et al., 2009; Durier et al., 2019a; Tsukamoto et al., 2020; Durier et al., 2021), while Sr isotope analyses are even more rarely applied except on woods (Bernabei, 2020).

1.2. Objectives

- Contribution to the knowledge of the history of uses of musical instruments

This PhD aims to develop a feasibility study on the contribution of: i- ¹⁴C geochronology and ii- organic and Sr geochemistry, respectively to deepen scientific knowledge on: i- the dating and ii- the geographical provenance of the materials of musical instruments. The long-term perspective is to tackle the issues of counterfeiting, retouching, maintenance, (musical) use and restoration of instruments, in order to study the long material history of musical instruments since they emerged from the workshops, and to identify the geographical origin of the materials used for instrument making. In summary, two major questions are raised here about the composite parts of musical instruments: i- when were they manufactured or restored? ii- where did they come from or where were they restored? Among the natural materials used for the

making of stringed instruments, varnishes (including their organic compounds) and gut strings were studied during this PhD since varnishes retain stratigraphic and surface traces of uses through time, while strings were often replaced during musical use; they are both, therefore, a testimony of the material history of musical instruments.

- Focus on linseed oil/colophony varnishes

Several PhD studies have been previously conducted on varnishes of musical instruments, including instruments kept at the Musée de la musique (Échard, 2010; Daher, 2012; Tirat, 2015). This PhD focused on early linseed oil/colophony varnishes that have been abundantly investigated as mythical varnishes of 17th-century Italian violins. Since varnishing practices were applied beyond the field of instrument making, the feasibility study using ¹⁴C dating was extended to other Heritage objects. The feasibility study using geochemistry was developed on organic ingredients of varnishes focusing on linseed oil and colophony (a similar approach would be possible for other natural resins such as shellac, benzoin, etc.).

1.3. Initial PhD plan

State-of-the-art

A state-of-the-art was first conducted on early varnishes in violin making using both a historical and a physico-chemical approach to their composition, application methods or maintenance practices with a view to applying ¹⁴C geochemistry (Echard 2010). Original and successive varnishes are traditionally preserved on musical instruments. The various layers were subjected to dust, natural ageing, wear, damage, revarnishing, restorations, etc. The review includes the chemical characterization of linseed oil and colophony before and after the heating, drying and aging processes of the varnishes (Tirat 2015). The dating of successive early varnishes is poorly documented, unlike their physico-chemical characterization.

Another state-of-the-art was conducted on the natural resins commonly used in violin making to study their geographical provenances including their elemental and organic composition with a view to applying organic and isotope geochemistry. Biomarkers as well as stable isotopes and multi-elements are indicators of geographical traceability (Regert et al., 2008; Liu et al., 2019). In the meanwhile, a historian conducted research on the socio-economic context of the production of early varnishes and colophony during the modern period in France (Weckerle, 2020, unpublished report). The geographical origin of natural oils and resins is poorly documented historically compared to inorganic ingredients such as pigments and driers in early varnishes.

Protocols

During this PhD, the multidisciplinary framework combined ¹⁴C geochronology and geochemistry with museum expertise including material characterization techniques. The initial methods investigated in this study were divided into three parts:

- Feasibility study of ¹⁴C geochronology

The first step was to search for and adapt micro-sampling tools suitable for ¹⁴C dating on successive varnish layers. Then, protocols using chemical treatments and carbon extraction were adapted prior to ¹⁴C dating for early varnish layers and gut strings.

- Feasibility study of organic geochemistry

A feasibility study was carried out on the application of molecular ^{14}C dating on linseed-oil and colophony using GC-Prep prior to ^{14}C dating. The tests lasted 3 months but could not be applied in the end, as confirmed later by the parallel bibliographical research which highlighted the complexity of retrieving uncontaminated original molecules of each organic compound in linseed oil/colophony mixtures. The results we obtained and the progress of our reflection on this issue have been reported in [Appendix 1](#).

- Feasibility study of isotope geochemistry

During this PhD, Sr isotopy was finally selected and tested to trace the geographical origin of organic binders. A bibliographical study was conducted to explore their main organic chemical components and inorganic elements at major, minor and trace levels. The Sr isotope analytical approach was developed and tested on colophony and linseed oil/colophony mixtures.

Material corpus

After the state-of-the-art studies, the search for a material corpus of "calibration" and "application" on which ^{14}C dating and Sr isotope measurements could be applied on early varnishes and natural binders respectively lasted more than 3 months.

1.4. Actual PhD plan

Due to the successive pitfalls that had to be dealt with in the course of this research, an atypical plan for this PhD was adopted.

State-of-the-art

The bibliographical research is two-fold with a historical ([Chapter 1](#)) and a physico-chemical ([Chapter 2](#)) approach essentially on early linseed-oil/colophony varnishes and their organic compounds. This step was paramount to define a material corpus and to better apprehend the complexity of the stratigraphies of early varnishes.

Protocols

The methods investigated in this study were finally modified and divided into two parts without the ^{14}C dating study at molecular scale.

- Feasibility study of ^{14}C geochronology ([Chapter 3](#))

^{14}C dating was applied on early "bulk" varnishes (with inorganic and organic compounds) previously separated into successive varnish layers using suitable tools for micro-sampling. Protocols were adapted using chemical treatments and carbon extraction prior to ^{14}C dating. The application on a wide material corpus of early varnishes and gut strings from Heritage objects revealed the achievements but also the pitfalls of the method.

- Feasibility study of Sr isotope geochemistry ([Chapter 4](#))

The tests using Sr isotope measurements were carried out using the protocols routinely used at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Saclay, France on archaeological samples. The main objective explored was to validate the postulate that the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope signature remains unchanged between the geological bedrock, the resin produced by the tree, and the colophony distilled by humans in order to use this isotope ratio as a marker of provenance of the organic natural resins used in violin making. The method tested on a wide range of raw materials demonstrated its potential use in Heritage science.

Material corpus ([Appendix 3 and 6](#))

The material corpus of “application” for ^{14}C dating measurements on early linseed oil/colophony varnishes of musical instruments was extended to lacquered pieces of furniture and horse-drawn carriages, mostly from the early 18th c. ([Chapter 1, Appendix 3](#)). as their original and successive layers of varnish are traditionally preserved as for musical instruments, unlike varnishes on easel paintings. The material corpus of “calibration” for Sr isotope measurements included soil, raw pine resin, colophony and linseed oil samples mainly from France ([Chapter 4, Appendix 6](#)).

This PhD study was possible thanks to the expertise of museum professionals (e.g. CRC UAR3224, Paris) and specialists in ^{14}C geochronology and geochemistry at the LSCE (CEA-CNRS-UVSQ, Gif-sur-Yvette, France) based on proven protocols and equipment run by technicians.

CHAPTER 1. European varnishes between the 17th and the 19th c.

1. Introduction

This chapter first presents the place of varnishes, among other materials used for stringed instrument making, that have been subjected to traces of use through time. The historical approach developed here is one of the tools that may contribute to dating and provenance studies of early varnishes of the modern period (from the 16th to the 19th c.).

A state of the art on European varnishes from the 17th to the 18th c., their compositions, applications, maintenance and restoration practices helped to pinpoint the material corpus and strategies for sampling Heritage objects of use in the framework of this PhD. A consistent starting point for this literature review was work performed on varnishes of musical instruments, including instruments from the Musée de la musique (Paris) collections, especially on linseed oil/colophony varnishes (Échard 2010; Daher 2012; Tirat 2015). The corpus of this research was extended from stringed instruments to lacquered furniture and carriages from the early 18th c. in view of the fact that coatings such as “Martin varnishes” comprising linseed oil/colophony were applied on a wide range of objects (Forray-Carlier and Kopplin, 2014).

Another aspect addressed in this chapter is the industrial production of varnishes and their compounds (especially turpentine and colophony) in order to gain greater insight into their dating and geographical origins. This report is mainly based on work carried out in the field of the history of technology at the Musée de la musique by Marion Weckerle regarding resinous products used by luthiers during the 18th c. in France¹.

The chapter comprises four parts: a short overview on musical instruments including their uses and their materials (part 1), a brief definition of early varnishes and their composition, their application and their material history with a focus on European linseed oil/colophony varnishes, furniture and sleds (part 2), a socio-economic contextualization of the production, trade and storage of colophony, turpentine and varnishes used by artisans from the harvesting of pine products to the application of varnishes on objects (part 3), and a description of the other materials besides varnishes used in violin making impacted by the different uses and associated with issues of dating and provenance (part 4).

2. Overview of the use and materials of stringed instruments

2.1. Musical instruments as an object of use

In his famous book *The Origin of Musical Instruments*, the ethnomusicologist André Schaeffner (1936, p.9) investigated the relation between music made by people throughout the world and

¹ Unpublished report accessible at the Musée de la musique, « Recherches pour une histoire appliquée de la colophane à archet » mweckerle@cite-musique.fr marion.weckerle@gmail.com

the sound objects used to produce music. Musical instruments can be defined as both art objects and objects of (musical) use which are or were developed dependently on a soundscape. They spread in different cultural environments and were adapted through musical tastes and practices, geographical regions and historical periods.

The early musical instruments studied in the framework of this PhD are classified among the chordophones (Von Hornbostel and Sachs, 1914). The different stringed instruments such as bowed instruments, keyboard instruments, plucked instruments, which are named according to the different mode of excitation of the strings, have the same principle for producing sounds: an interface with the instrumentalist (fingerboard, keyboard, ...), a string tension control system (peg system, tuning pins, nut, ...) and a resonance block or structural parts (body, soundboard, bridge, resonator, ...). The instrumentalist controls the radiated sounds resulting from the excitation of the strings or resonant system excited by a hammer blow, a pluck, a continuous friction and coupled with the sound body or radiant system (Figure 1, a).

After their making, musical instruments underwent alterations, cleanings, replacements, additions, modifications, restorations or even forgeries during their long material history. Indeed, musical instruments as objects of use are regularly "maintained" in playable conditions. Modifications are inherent to any musical use which implies for example changes imposed by new cultural standards, revarnishing or the replacement of parts subject to wear such as bridges, necks or strings. The absence of modifications is inherently suspicious and we may question the authenticity or representativity of an unaltered early instrument.

2.2. Organic materials for instrument making

Over the ages, almost every material in nature has been made to vibrate in order to produce music by different cultures (Rault, 2000). Schaeffner (1968, p.126) states that from one material to another, instrument making succeeded in embracing almost all nature². Some cultures even use classifications of musical instruments that are based on construction materials (Picard, 1996) rather than on playing methods.

Wooden musical instruments are complex and composite sound producing artefacts, comprising numerous organic components, which implies that the materials for instrument making mainly come from trees and animals (wood, silk, gut, resins, etc.). If we concentrate mainly on the instruments of the string quartet (Beament, 2000; Bucur, 2016) (Figure 1, b):

- i- wood is the main material used for the instrument body and the different parts such as the bridge, soundpost or tailpiece;
- ii- glue holds the parts together;
- iii- varnishes and their ingredients (including natural resins) protect the instrument;
- iv- unwound gut strings were used at least until the beginning of the 20th c. and today again by baroque ensembles;
- v- the bow is made of wood, horse hair and requires colophony;

² "De matière en matière, la facture des instruments est arrivée à embrasser à peu près toute la nature."

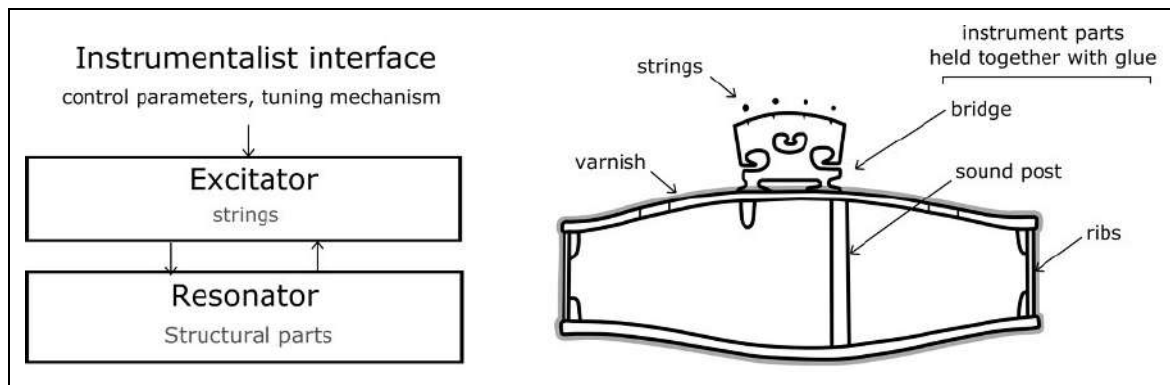


Figure 1. From the left to the right a) Playing principle of stringed instruments b) Transversal cross-section of a violin as an example of stringed instruments with a description of the mounting, glues, strings, and varnishes.

Early (European) stringed instrument making is an artisanal practice that also belongs to a wider socio-economic context including the sourcing of materials, supply networks, modes of production, consultation/relations between instrument makers and other actors for the realization of the sound object. It depends first on the availability of territorial material resources such as wood. Then comes the market with the various suppliers; instrument makers source their raw materials based on the desired quality and the affordability (Clarke, 2017). The production of the object by violin makers draws from various other fields: wood suppliers, resin makers, string makers, colour sellers, apothecaries, etc. According to the geographical and historical context in which they were made, the mode of production of the instruments also depends on the available techniques, including storage practices.

2.3. Materiality as a source of information

Stringed instrument making is imbued with a long tradition of oral practices and transmission. As a result, musical instruments and their material history are seldom associated with extensive and sufficiently detailed direct written sources. Moreover, although stringed instrument making and especially violin making is still marked by tradition³, current making practices cannot be used as references to study and retrieve early practices. Hence, material analyses of the different components of early musical instruments are an important source of documentation.

Surviving written sources might a priori be used to situate an instrument or a family of instruments in music history, to identify successive changes, or even the appearance of a "new" instrument that enriched the *instrumentarium* of a culture, but experience shows that written sources are very problematic from a methodological point of view. The (European) violin is a good example, for which one of the first citations is due to Philibert Jambe de Fer, a musician and theorist active in Lyon (France) in the middle of the 16th c. Unfortunately, this author defines the instrument only from a sociological perspective, in opposition to other instruments, specifying that the violin is very different from the viola da gamba⁴, but he does not provide

³ The violin family has been widespread in Europe since the 17th and 18th c. In Italy, the instruments were usually made according to the Cremonese method, with a mould, which is still in use today. North of the Alps, however, freeform (mouldless) violin making was the most common way to build a violin until the 18th c. Karel Moens, "Die frühe Geigenbau in Süddeutschland", in *Studia organologica. Festschrift für John Henry van der Meer zu seinem fünfundsiebzigsten Geburtstag*, Friedemann Hellwig (ed.), Tutzing, 1987, p. 349-388.

⁴ « Le violon est fort contraire à la viole... » Philibert Jambe de Fer, 1556, *Epitome musical des tons, sons et accordz*, Michel du Boy, MDLVI, Lyon, p. 61

any morphological information. Written sources also induce terminological issues, as the words used do not necessarily have the meaning they have today. For example, the French word "violon" is attested since at least 1523, but it is impossible to accurately ascertain the morphology of the object to which it referred at that time⁵ (Ceulemans, 2011).

The availability of written sources about the provenance of materials supplied for early instrument makers is similarly limited due to oral tradition, such as that for the wood used in violin making⁶.

Regarding the material history of early stringed musical instruments, the chronology of past alteration-modification-restoration processes undergone by a particular instrument is seldom recorded in written reports. As common artisanal practices inherent to the life of instruments, maintenance and repairs were mentioned in violin making treatises (Maugin et al., 1894; Tolbecque, 1903; Greilsamer, 1910), while a few past alterations and restoration interventions were summarily reported on musical instruments from private collections or museum collections before the past few decades⁷. For example, Vandervellen (2017) reported the material traces of earlier interventions on musical instruments kept at the MIM, Brussels.

Currently, the issue as to whether past restorations should be removed or whether on the contrary historical traces should be preserved as material documentation is still debated in museum institutions. Material analyses can be used to identify chronological markers of successive modifications and to study the provenance of heterogeneous materials from earlier stringed instruments.

3. Varnishes

Varnishes were presumably applied for both protection and aesthetic purposes on musical instruments and other Heritage objects such as easel paintings, scientific instruments, pieces of furniture, horse-drawn carriages, etc. Their raw materials were of natural origin such as natural resins - mainly plant exudates - before the emergence and industrial development of synthetic varnishes in the second half of the 19th c. and the early 20th c. The successive historical uses and interventions on Heritage objects yielded a complex varnish stratigraphy comprising heterogeneous materials from different periods, material traces of alteration and maintenance practices. The identification of original or retouched areas on objects of use requires a good knowledge of their historical context and use.

The terminological distinction between "varnish" and "lacquer" remains unclear even today, and is controversial despite their widely discussed etymological origin (Cattersel, 2019). Both words covered a wide range of techniques in the past, often related to the same kinds of

⁵ «La plupart des auteurs citent comme occurrence la plus ancienne les comptes du trésorier général du duc de Savoie, qui font état, le 17 décembre 1523, d'un paiement de six scudi « pour les trompettes et vyollons de Verceil [la ville italienne de Vercelli] »», Ceulemans, A.-E., 2011, p. 38.

⁶ Houssay, A. *Choix et traitements des bois pour la facture instrumentale* [Sous la direction de Liliane Hilaire-Pérez]. Université Paris Diderot - Paris 7. The subject initially concerned the origins of the wood used by early Parisian makers but the author had to extend the research scope due to the lack of available written sources (personal communication, 2017).

⁷ Ignazio Alessandro Cozio di Salabue (1755-1840), *Carteggio, trascrizione di Renzo Bacchetta*, Milano, A. Cordani, 1950.

Sébastien-André Sibire, *La Chélonomie, ou, Le parfait luthier*, Bruxelles, Weissenbruch, 1823, p. 128-129.

ingredients: natural resins, gums, drying oils, essential oils, alcohols, driers, pigments. A current trivial distinction is based on the level of transparency, which defines “lacquer” as opaque and “varnish” as transparent. “Martin varnishes” produced in early Parisian varnish workshops are a relevant illustration of the interchangeability of the terms as they are clearly categorized as a European lacquer imitating Asian lacquers. To avoid confusion in the following, the term “varnish” is mainly used for (European) violin making, “lacquer” for European and Asian lacquers and “coat” for carriages.

3.1. Generalities on early European varnishes

The earliest material traces of varnishes on European stringed instruments date from the early 16th c., as identified by museum expertise on the instruments manufactured by Laux Maler (c.1480-1552) (e.g. lute, Laux Maler, 1529-1552, Bologna, coll. Musée de la musique, inv. n°. E.2005.3.1)(Echard, 2006). However, an earlier use of varnishes cannot be excluded. Varnishes in violin making initially covered only some parts of the instrument; their origin and role are currently not completely defined.

Early recipes of natural varnishes used in Europe between the 15th c. and the 19th c. were gathered during previous research. The Musée de la musique hosts an online database named VERNIX (Malecki, 2006; Echard and Malecki, 2012) which contains 368 historical recipes from 18 sources between the 15th c. and the 18th c. In the framework of the European Lacquer in Context project (ELinC2018), Cattersel (2019) collected 1050 recipes of European lacquers (including recipe variations) from 51 historical sources dated from the 15th c. to the 19th c. As part of the LacCa project, Schröter et al. (2019) also gathered early recipes of natural varnishes mainly from the 19th c. The pre-industrial composition of varnishes in Europe through the modern period depends on a large panel of factors such as workshop practices and personal maker preferences, the trade and availability of materials, market demand or the nature and function of the object, which are studied by the discipline of technical art history using a large panel of scientific disciplines and tools.

According to Malecki (2006), early varnishes that mainly comprise an organic fraction are categorized as follows: oil-based, alcohol-based and essential oil varnishes. A statistical treatment of early recipes listed in the VERNIX database showed a tendency towards an increasing number of alcohol-based varnish recipes during the 18th c. (Figure 2). Despite current methodological limits using written sources, a material-technical overlap has been suggested between varnishes for violin making and easel painting related to the popularity of alcohol varnishes over oil-based varnishes due to changes in distillation processes, shorter drying time and increasing demand and production (Perego, 2006).

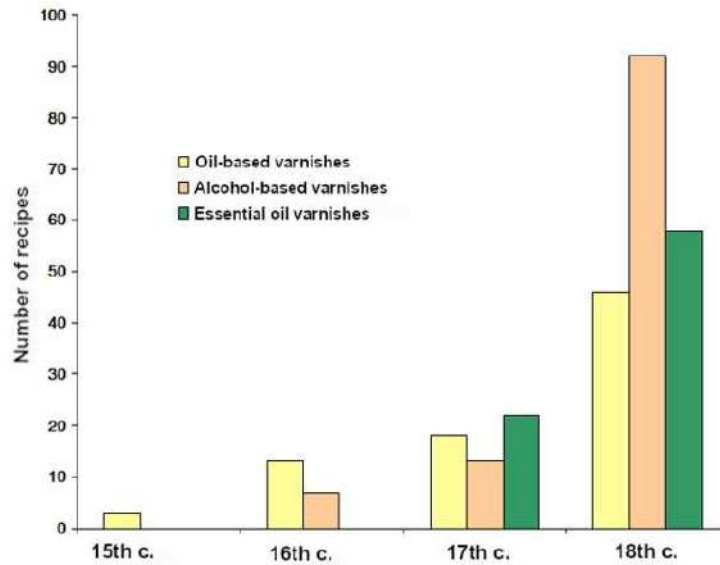


Figure 2. Evolution of the different types of varnish among 368 recipes dated between the 15th and 18th c. listed in the VERNIX database (adapted from Malecki, 2006)

According to Cattersel (2019, p.32), early varnishes can be categorized into 4 categories: i- solvent based varnishes (including alcohol varnishes but also essential-oil varnishes); ii- oil-based varnishes requiring the addition of a drying oil such as linseed oil; iii- resin based varnishes (heated resin for application with no solvent required) ; iv- protein based varnishes (including collagen glues such as hide or sturgeon glue dissolved and heated in water) (Figure 3). As reported by Malecki (2006), a similar popularity was achieved by spirit-based varnishes especially in the 18th c. according to a statistical treatment of the early recipes listed in Figure 3. Spirit-based recipes are expected to be easier and cheaper to make for an amateur audience compared to oil based varnishes. However, doubts subsist about the studied sources which are not completely attested as being related to the professional context.

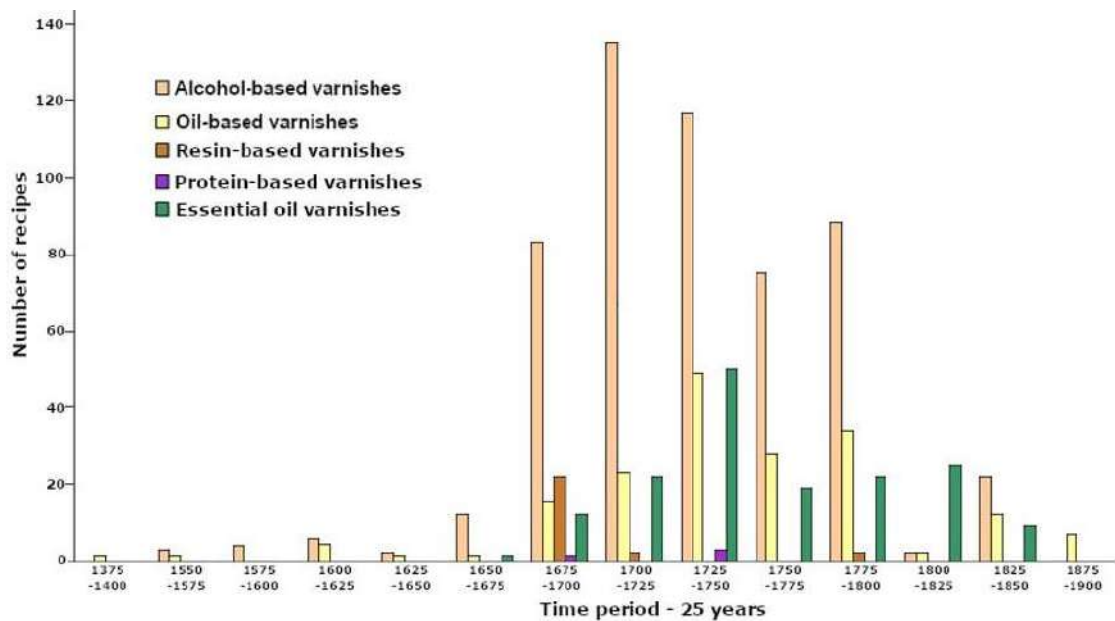


Figure 3. Evolution of the different types of varnish among recipes dated between the 15th and 19th c. reported by Cattersel (2019)

This PhD study focuses on linseed oil/colophony varnishes which are the most widely studied by instrument makers, restorers, curators and physical chemists, such as the varnishes applied to the famous Italian violins of the 17th c. These varnishes are particularly rich in carbon, containing a mean of 70 wt% C according to tests done with the elemental analyzer at the LSCE with the aim of applying ¹⁴C dating. However, linseed-oil/colophony varnishes on early stringed instruments which could provide interpretable data using ¹⁴C measurements are scarce i.e. with a production period within the following range of dates: [1600 - 1730] or [1770 - 1810]. Thus, the initial corpus of musical instruments was extended to other Heritage objects including horse-drawn carriages and pieces of furniture lacquered with original linseed oil/colophony varnishes, as the same materials and artisanal practices were used on a large range of varnishes or lacquered objects by corporations of painters, gilders, varnishers, etc. during the 18th c. (Watin, 1773a), for example, as previously mentioned with the material-technical overlap between violin making and easel painting. The scope of this PhD led me to focus on Heritage objects for which the original varnish layers were traditionally preserved and which are also objects of use with traces of their material history in the successive varnish layers. In fact, original varnishes were also usually preserved on musical instruments, early horse-drawn carriages and pieces of furniture (Mills and White, 1987). However, despite the abundant use of oil and turpentine, early easel paintings were not studied here as the yellowish original varnishes were generally removed and later replaced for aesthetic reasons.

Based on previous research and museum expertise (Échard, 2010; Augerson, 2011; Forray-Carlier and Kopplin, 2014; Cattersel, 2019), it was possible to identify objects from museum and private collections which were expected to be coated with original linseed oil/colophony varnishes from the 17th and 18th c.

European lacquers were applied on a large range of objects in imitation of Asian lacquers but other materials such as tortoise shell, minerals (aventurine, marble, lapis lazuli, granite, ...) were also used. The importation of lacquered objects began with the trade between Portugal and Japan in the 15th c. (Huth, 1971; Webb, 2000; Kopplin, 2010). Asian lacquers were luxury products commissioned by wealthy customers. Owing to the growing demand of the European market in the 18th c., European artisans appropriated the technique, adapted it to the tastes of European society, and freed themselves from increasingly expensive Japanese and Chinese exports monopolized by Holland. Famous varnish makers emerged in the late 17th c. such as the Dagly brothers (Gérard, 1600-c.1715 and Jacques, 1665-1728), known especially for lacquered *bois de Spa*, whose traditional recipes contain ingredients such as oil, shellac, turpentine or sandarac (Steyaert et al., 2019). The Parisian merchant and mercer Thomas-Joachim Hébert (1687–1773) is known to be one of the first to commission pieces of furniture made from cut and refitted Japanese panels and/or Chinese panels, at least since 1720 (Forray-Carlier and Kopplin, 2014). From c. 1730 on, the Parisian Martin brothers (Guillaume, 1689-1749, Etienne-Simon, 1703-1770, Robert, 1706-1765) acquired a high reputation throughout Europe thanks to their famous varnishes, whose decline came after 1850. According to physico-chemical analyses, Martin varnishes comprise oil and colophony compounds (Forray-Carlier and Kopplin, 2014).

Previous research has been conducted on pre-industrial coatings of horse-drawn coaches (Augerson and Demailly, 2001; Rommelaere, 2008; Augerson, 2011; Forray-Carlier and Kopplin, 2014). However, to our knowledge, few physico-chemical analyses on their stratigraphy have been published except on the sled “Le patineur” kept at the Château de Versailles (Augerson and Demailly, 2001). Oil-based varnishes were used until the end of the 19th c. because of their

weathering resistance properties. Early varnishes comprise oil and colophony as cheaper components before the increasing popularization of oil/copal varnishes c.1730-50 (Augerson, 2011).

- Based on the literature and museum expertise, and given the common materials and artisanal practices, I broadened the corpus of early varnishes on musical instruments by including lacquered furniture and horse-drawn carriages with original early varnish/lacquer layers presumably dating from the early 18th c.

3.2. Early varnishes in violin making

3.2.1. Historical context in Europe between the 16th and 19th c.

Between the 16th and the 19th c., different categories of varnishes were used in violin making. A general landscape is suggested here although the dominance of one category compared to another, depending on violin making centers and historical periods, is necessarily subject to discussion. Echard (2010) reported the following conclusions on varnishes in lutherie between the 15th and the 19th c.

- The composition of varnishes seems to be related to the geographical distribution of the main early violin making centres in Europe (Figure 4):
 - o linseed oil-colophony varnishes in Italy
 - o oil-shellac varnishes mainly in Paris
 - o shellac varnishes, occasionally in Paris, Barcelona and Germany
- During the 16th c., mainly oil-based varnishes were applied on bowed instruments. Shellac varnishes were introduced in the 17th c., imported by the Jesuits from Asia ([Chapter 2 – § 3.7](#)) as observed on the French “bass viol”, Collichon, 1683, coll. Musée de la musique, E.980.2.667. During the 18th c., two types of varnish competed: alcohol-based varnishes and oil-based varnishes, as a technological breakthrough in alcohol distillation favoured the increasing use of alcohol-based varnishes. During the 19th c., oil-based varnishes were reinvented by influential violin makers to retrieve varnish recipes of the 17th c. Italian masters.
- Oil-based varnishes are made of vegetable oils and natural resins, with the optional addition of metallic salts and pigments.

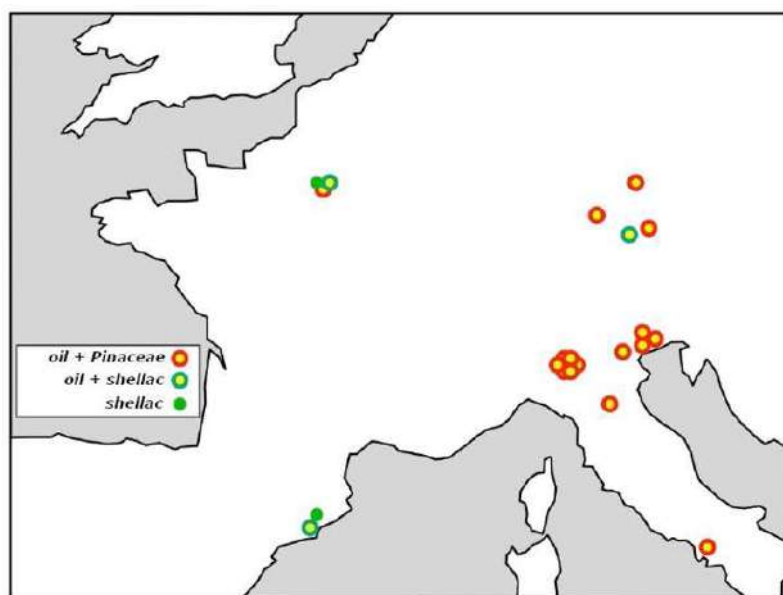


Figure 4. Chemical composition of original varnish layer on the musical instruments analysed by Echard (2010) according to the location of the workshop in Europe.

3.2.2. Use and maintenance of varnishes

For their application on musical instruments, varnishes were dissolved in highly volatile solvents such as ethanol or turpentine. After the solvent had evaporated, the thickness of the dry film was usually around 30 μm (20-50 μm) (Échard, 2010; Tirat, 2015). The original varnish was commonly applied in 2 or 5 layers on bowed instruments.

Over time, the varnish surface tends to become yellowish and brittle with the appearance of a network of cracks due to the inherent mechanisms of natural ageing, including photo-oxidation, which alters the chemical structure and compounds of the varnish layers (Azémard, 2014). The varnish surface also usually underwent wear and tear during the musical use of instruments, occasional impacts, blows, and intentional modifications by violin makers such as re-cuttings and re-varnishing.

While varnishes on paintings are usually removed and replaced, original varnishes are traditionally kept on musical instruments, which is also true for furniture, horse-drawn carriages or early scientific tools. Maintenance practices in violin making consisted in visually retrieving the homogeneous appearance of the original varnish using compatible materials. The violin maker traditionally passed a cloth or a pad soaked with oil or shellac dissolved in alcohol over the worn varnish with controlled gestures causing the abrasion and transport of material that smoothed the surface of the varnish. While these interventions are still recommended today by violin makers⁸, they are not among practices applied in the museum context. In violin making, the worn parts of varnishes were often retouched using binders with a higher concentration of pigmented particles, such as iron and manganese-rich earths and ochres (Échard, 2010).

The resulting stratigraphy of early violins is complex to study because of the non-uniform wear of the varnish and subsequent layers of maintenance, inducing surface and thickness heterogeneity. The varnish stratigraphy has been shaped over time with successive layers

⁸ Hans Weisshaar and Margaret Shipman, *Violin Restoration. A Manual for Violin Makers*, Los Angeles, 1988, p. 199-210, a manual used for example in the Ecole de lutherie of Gauthier Louppe.

affected by dust, natural ageing, damage, retouching, re-varnishing, restorations, etc. Thus, the varnish surface is a testimony of the material history of musical instruments.

Figure 5 shows an example of a historical varnish stratigraphy (Échard, 2010).

- 1- Ground: an optional layer of proteins such as animal glue or of mineral compounds such as gypsum, talcum, clay, etc. Its presence or absence, and its composition depend on violin making schools over time or the wood species. Musical instruments made of woods with a lower permeability such as spruce, maple or ash seem to be devoid of this ground layer.
- 2- Varnish
- 3- Dirt
- 4- Natural ageing of the varnish
- 5- Anthropogenic actions: wear and tear, alteration, re-varnishing, etc.

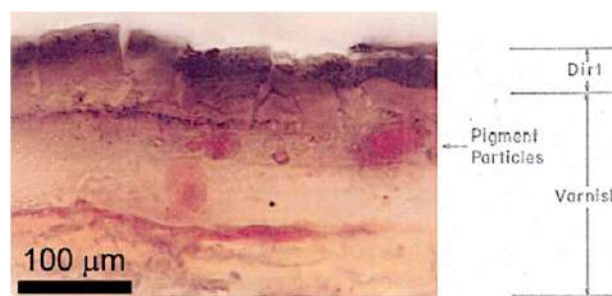


Figure 5. Stratigraphy of a varnish sampled on a Goffriller cello, National Gallery of Art, Washington DC (Condax 1970) (from Echard, 2010).

3.2.3. Linseed oil/colophony varnishes

Since the 1990s, numerous analyses have been carried out on Stradivari's violins (Brandmair et al., 2010; Bucur, 2016) in order to reveal the mystery of the legendary forgotten recipe of the earlier Italian masters' varnishes. According to current knowledge, the Old Cremonese makers of the 17th c. (Amati, Stradivarius, Guarneri) employed a varnish based on linseed oil and a distilled Pinaceae resin, which are common and cheap ingredients in Europe. It is widely acknowledged that the proportion of linseed oil/colophony attributed to Stradivari's varnishes is 70:30 (Weththimuni et al., 2016).

Consequently, as mythical varnishes of 17th-c. Italian violins, linseed oil/colophony varnishes have been abundantly investigated from both historical and physico-chemical points of view. Several PhD studies have been conducted at the Musée de la musique (Echard 2010; Tirat 2015). This knowledge base is of great interest to develop a feasibility study of the application of ¹⁴C geochronology and geochemistry on varnishes.

¹⁴C dating could not be applied on 17th-c. violins for specific conservation issues. Thus, knowing that ¹⁴C dating provides more reliable values in the following range of dates during the modern period: [1600 - 1730] or [1770 - 1810], the constitution of a material corpus of early varnishes focused on 18th c. stringed instruments although the probability of finding oil-based varnishes would be higher during the 19th c.

- The original varnish layers were traditionally preserved. The final varnish coating is a testimony of the history of the (musical) use in its composition and its stratigraphic and surface distribution.
- The composition of varnishes in lutherie has been widely studied in the literature with a special focus on the Old Masters' Italian varnishes comprising linseed oil/colophony varnishes (Bucur, 2016).

3.3. Early coatings in horse-drawn carriages

3.3.1. Historical context in Europe during the 18th c.

Rommelaere (2008) reported that research on European carriages from the modern period has intensified during the past decades through the study of a corpus of several hundred surviving carriages and through the examination of early treatises (Garsault, 1756; Roubo, 1769; Watin, 1773a), almanacs and business repertories or catalogues. This recent research evolution mainly reviews the historical context, the successive technological breakthroughs, stylistic influences, changes in professions, practices and trade from the 18th c. to the 19th c. A relative dating of 18th c. carriages is possible based on the comparison of stylistic features, as they were related to decorative arts or architecture. From the late 17th c. to the mid-18th c., France dominated European production, with carriages as a luxury furniture. A new fashion came from England in the middle of the 18th c. for simpler horse-drawn coaches used as a common means of transport. This tendency was favoured by the French Revolution and the beginning of industrialization at the end of the 18th c. (Rommelaere, 2008).

Few articles are available on pre-industrial coatings of carriages (whether they were mounted on wheels or runners) before the pivotal period between the 18th c. and the 19th c. in Europe (Augerson and Demailly, 2001; Augerson, 2011). However, dissertations and reports from restorers are available (Devergne, 1993; Wegwitz, 2010; Huber, 2016; Hinckley, 2017). In this research, I studied mainly coatings from sleds and one Berlin carriage. Sleds, sledges and sleighs are vehicles that are mounted on runners for travelling over snow or ice (Figure 6). Horse open sleighs with rich and fanciful decorations became fashionable in European aristocratic society for showing off in northern countries such as the Low Countries, Sweden or Russia around the 17th c. and the fashion spread to France in the 18th c. A Berlin carriage is a four wheeled vehicle whose body is suspended on rails, designed for passenger transport on the roads.

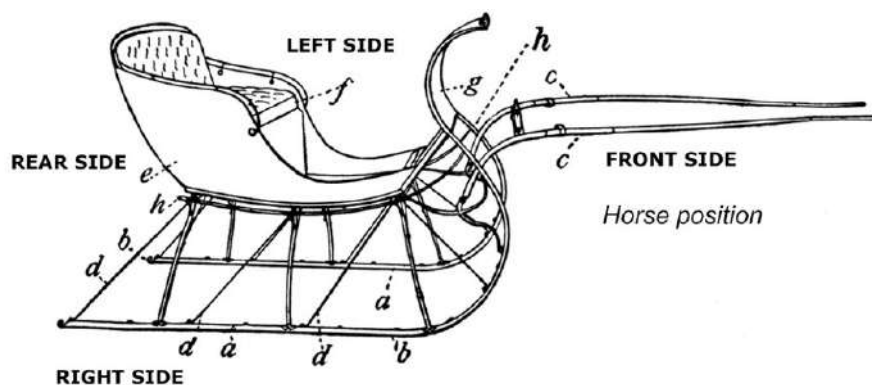


Figure 6. Schematic of an early sled with the designation of the different parts and their orientation according to the direction of travel: a) runners b) shoes c) shafts or thills d) braces e) body f) cushioned seat g) dashboard h) raves (adapted from Whitney, 1889)

- *Rail: a slender wooden member used in the construction of a vehicle body, usually running the length or width of the body.*
- *Rave: a longitudinal piece above the knees of a sled, joining with the runner in front.*
- *Braces, cross-beams, stanchions*
- *Knees: erect wooden supports running upward from the runners of a sleigh or sled.*
- *Gear: the underpart or running part of a vehicle, including axles, springs, fifth wheel, wheels, etc.*

3.3.2. Use and maintenance of coatings

What are the known artisanal processes and materials used for coating horse-drawn coaches? How was the coating stratigraphy made? What materials were used?

The application of the coatings on carriages traditionally followed several main steps: 1-priming coats, 2-rough coats, 3-putty and guide coats, 4-color coats, 5-glazes, 6-varnish coats (Wegwitz, 2010; Augerson, 2011; Hinckley, 2017)(Table 1). The first three coats correspond to the preparation layer applied on the wooden support of the carriage. The putty and guide layers aim to remove imperfections by pumicing so that they hardly appear in the final stratigraphy. The decor layer comprises the colour coats including pigments with a good covering power (which contribute to the final hue) and glazes including pigments with a low opacity (which increase the colour depth). The painters and gilders had a wide range of ground techniques available such as: Aventurine ground, gold ground, or with paillons (tiny motifs cut in thin gold or silver leaves). The upper varnish coats comprise rubbing varnishes and a finishing varnish which are removed for the application of new decors through the successive periods of use of the carriage (Devergne, 1993). The protective varnish layers should be resistant enough for rubbing thanks to the addition of natural resins. Early European carriage painters had a long tradition of use of linseed oil/colophony varnishes before the latter were supplanted by the harder copal resin in the mid-18th c. The polishing technique consisted in sanding successive thin varnish layers with lead white, linseed oil and pumice, leaving traces of lead that were useful to reduce the yellowing of diterpenic resins with time (copal, colophony) (Augerson, 2011).

Table 1. Table of stratigraphy and composition traditionally used in coatings on carriages

Main coats	Steps of application	Composition
Varnish	Finishing varnish	linseed oil + natural resin + lead white (for siccative properties and to avoid yellowing)
	Rubbing varnish	
Decor	Glazes	Transparent oil colours
	Color coats	Opaque oil colours
Preparation layers	Putty and guide layers	-
	Rough layers	2/3 linseed oil + 1/3 turpentine + 2% siccative + yellow and/or red ochres (English filling) + lead white
	Priming layers	1/4 linseed oil + 3/4 turpentine + lead white and/or chalk

The application of coatings was traditionally treated separately on the body and the undergear with a simpler stratigraphy on the runners.

Horse-drawn coaches were both artwork and an object of (transport) use. Coatings underwent maintenance and adaptation to aesthetic tastes during the period of use of the carriages. Mud or dust deposits were abundantly washed with water and coated parts affected by shocks and wear and tear were renovated. The successive decors were applied one on top of the other through time and were seldom removed (Devergne, 1993)(Figure 7).

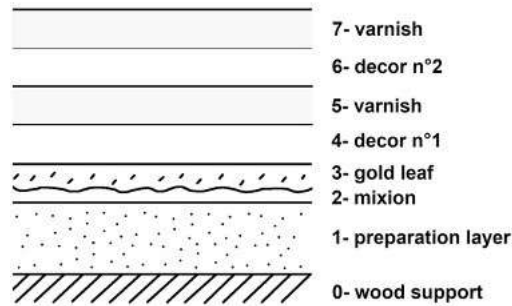


Figure 7. Schematic example of an application of successive early coats on carriages through time

In the museum context of indoor conservation, the protection of coatings was optimized by more or less durable varnishes according to the period of interventions such as beeswax, paraffin, linseed oil or petroleum derived varnishes. Worm-eaten parts were treated with insecticides based on petroleum derived products. During restoration interventions, dust is often removed with water-based solutions. A dammar/wax mixture or petroleum derived products for gluing coating chips, as well as occasional retouching with acrylic or water-based paints could have been used according to reports from restorers. Bronzine was particularly used in the nineteenth and early 20th c. to restore gilded objects. The operation is quick, without prior cleaning most often, and restores the shine to the object. Bronzine is composed of a metallic powder often based on copper sprayed on varnish or mixed with a binder and it can be found on the gilded surface of numerous objects.

3.3.3. Linseed oil/colophony coatings

Carriage painters encountered specific problems regarding the selection of suitable materials as horse-drawn coaches were subjected to weathering, shocks, vibrations, dust and mud during transport. Thus, oil-based varnishes were traditionally applied until the early 20th c. due to their weather-resistance and better mechanical resistance than alcohol-based varnishes. Carriage coatings were formed by numerous oil-based coats in order to improve their solidity, so the materials also had to be affordable and have siccative properties to reduce the cost and time of production. Colophony, despite its tendency to yellow and crack, meets these specifications. According to the literature, oil/colophony varnishes were used before the extensive introduction of oil/copal varnishes in the mid-18th c. (Watin, 1773a; Augerson, 2011). As with oil easel painting, the proportions of linseed oil, turpentine and diluted resin were adapted for the application of “thick on thin” binder layers, a traditional rule for the proper drying of the underlying layers and the adhesion of the upper layers.

An example of “Martin varnishes” is the Aventurine decor, a European imitation of the Japanese *nashiji* lacquerware. It consists of spraying copper flakes and/or other metals (gold, silver, bronze, brass, tin, ...) on a fresh oil varnish; resin and linseed oil were used as binders with the possible addition of asphalt, litharge, vermilion or turpentine (Watin, 1773a)(Figure 8). A protective alcohol-based shellac layer was sometimes previously applied in order to protect rough layers during the application of the oil coats, as well as for oil mixtion, to avoid the absorption of the oil mixtures by the preparation layers (Augerson, 2011).

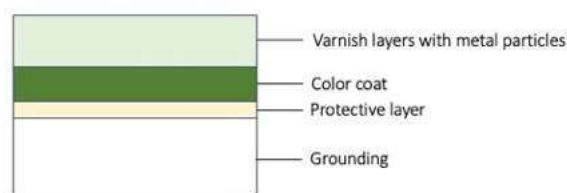


Figure 8. Schematic Aventurine decor belonging to a European lacquerware imitation of Asian techniques.

For gold decors, two main gilding techniques could be employed: 1- water gilding, which comprised two sub-categories: a) using a clay-based preparation layer named bole mixed with animal glue, or b) using a thin preparation layer mainly made of animal glue; 2) oil gilding: using an oil-based gold size layer, also named mordant or mixtion, to apply the metal layer (Wu et al., 2020)(Figure 9).

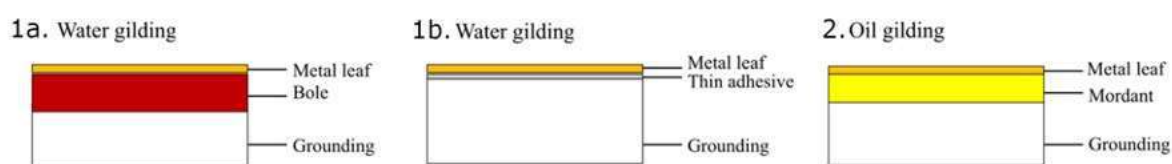


Figure 9. Schematic of different techniques 1a) water gilding with bole, 1b) water gilding with adhesive ground and 2) oil gilding (adapted from Wu et al., 2020)

Oil gilding was the most highly appreciated gilding technique on horse-drawn carriages from the 18th c. (Devergne, 1993; Wegwitz, 2010). Augerson and Demailly (2001) reported the use of an oil/resin mixtion (or mordant) to glue thin silver leaves on the coat of the sled “the skaters” (inv. T 767 C.1, c.1720, Coll. Château de Versailles). Water gilding has been punctually identified on the coach of Infante D. António (inv. V 0016, early 18th c., Coll. Museu Nacional dos Coches, Lisboa) (Hinckley, 2017). It is currently assumed that oil gilding supplanted water gilding as a more suitable technique after a technical breakthrough prior to the early 18th c.⁹

- Oil-based varnishes were used for their weathering-resistance on carriages. Linseed-oil/colophony varnishes were used prior to oil/copal varnishes which came into use c.1730-50.
- Oil/colophony mixtions were preferentially used for gilding decors in the early 18th c.
- “Martin varnishes” which were used on musical instruments, furniture or carriages, contained oil/colophony in the early 18th c.

3.4. Industrial and commercial practices around organic binders¹

The study of the dating and provenance of linseed oil/colophony varnishes questions the socio-economic context which encompassed: i- production, ii- trade and iii- appropriation of resinous products by violin makers (for varnishes and bow colophony) in 18th c. France¹.

Here, I will briefly contextualize the production environment. Changes progressively occurred in manufacturing organization during the 16th, 17th, and 18th c that led to developments of the 19th c. industrial revolution. Several French towns and villages were especially organized around

⁹ Personal communication Isabelle Devergne. Further material analyses on early varnishes from horse-drawn carriages would be necessary to support this research.

artisanal or industrial activities under the Ancien Regime when France was the foremost industrial kingdom in Europe. The turn of the 18th and 19th c. was marked by agricultural crises that generated manufacturing crises. In the late 18th c., the French Revolution dissolved corporations and promoted industry in the country (Delsalle, 1993).

3.4.1. Studies on the trade

Currently, studies on the trade of organic binders for varnishes combining written sources and/or material analyses are scarce in the literature in comparison with provenance studies on paint pigments (Thomas, 2016). Moreover, the terminology regarding resins and botanical names in early recipes can be ambiguous and lead to misunderstandings (Dietemann et al., 2019).

3.4.1.1. Colophony production centers in written sources

The provenance of pine products for violin making (varnishes or bow colophony) was seldom mentioned in written sources as their supply often took place at an interpersonal level. However, the main early exploitation centers of pine resin are documented due to major factors such as: i- control of the production and export of pine resin for their use in naval construction, ii- management of the forests during the wood crisis due to massive deforestation in the 18th-19th c. with the development of the Industrial Revolution, as testified by administrative documents such as handwritten decrees authorizing or prohibiting the export of pitch. The pine resin exploitations in France from the 18th c. onwards inventoried at the Musée de la musique included¹:

- resin harvesting and colophony manufacturing near Marseille as mentioned in a letter sent to the Royal Society in 1698 from Nîmes¹⁰
- historical production of resinous products in Gironde including turpentine, colophony and varnish. A source from 1778 in the historical archives of the Gironde department indicates through the travel diary of a factory inspector that turpentine was produced in factories in the Landes, then marketed for the production of varnishes¹¹. 100 pine resin exploitations in Gironde were listed in a statistical survey made in 1856¹².
- exploitation of maritime pines in Fontainebleau near the Rocher d'Avon in 1824-1826¹³
- exploitation of maritime pines in Gascony and Provence

Jaupart (1966) reported the flourishing export trade of resin products from Bayonne during the 18th c. In 1781, a merchant from Bayonne wished to export an extensive quantity of pitch, resin and tar to Portugal¹⁴. Dax in the Landes was a well-known market for pine products. According to Steigenberger (2013), written sources reported that “Bordeaux” turpentine and colophony

¹⁰ “The Way of Making Pitch, Tar, Rosin and Turpentine Near Marseilles; Communicated in a Letter from Nismes, by Mr. Thomas Bent, to Dr. Welsted”, *Philosophical Transactions of the Royal Society of London*, vol. 20, n°243, 1698.

¹¹ “L'industrie et le commerce en Guienne sous le règne de Louis XVI”, *Journal de tournée de François-de-Paule LATAPIE, inspecteur des manufactures, 1778.* (Manuscrit appartenant à M. Henri Latapie)

¹² Survey of the “bureau de la statistique générale de France” on the manufactures of pine resin in Charente-Inférieure, Gironde, Landes and Lot-et-Garonne, *Archives nationales*, F/20/745/1

¹³ Pines and resin of Fontainebleau. Events, fires: “police des forêts”, *Archives nationales*, O/3/980

¹⁴ *Archives Gironde*, C/1641-1781

were obtained mainly in Bayonne, near Bordeaux in “Teste de Buch”¹⁵, Marseille, Toulon, in “Guienne”¹⁶, Nantes, and “Roüan”¹⁷, whereas “Strasbourg” turpentine had a different provenance such as resin collected from firs in the Alps (Switzerland, North Italy)¹⁸.

3.4.1.2. Varnish suppliers, market, stores and their ingredients

The literature is more abundant on the trade of materials for painters than for violin makers (Kirby et al., 2010). Dutch painters were known to purchase their pigments from color sellers named *verfvercopere*¹⁹ and Venetian painters from color sellers named *vendecolori*, whereas Roman, Parisian and London painters preferred apothecaries. Painters’ guilds had social networks with dealers in painting materials and apothecaries (Warolin, 2016; Campbell, 2019). The accessibility of ready-to-use varnishes and their ingredients by Parisian violin makers has been studied at the Musée de la musique based on the account books of Parisian merchants in Archive collections from the 17th, 18th and 19th c. of the corporation of “mercier” trade guilds, color merchants and resin makers¹.

Apothecaries and druggists

Natural resins, including colophony, were sold by apothecaries since they were used for medicines during the modern period. As an example, the Vigani Cabinet with resins, gums and other chemical products collected by the Italian pharmacist Giovanni Francisco Vigani (c.1650-1712) from druggists in London with some occasional information on harvesting, manufacture and trade of the materials mostly imported to England (Steigenberger, 2013). Apothecaries also sold ready-to-use varnishes such as common Italian varnishes comprising linseed oil and *greek pitch* or *pece greca* as mentioned in the introduction by Merrifield (1849), which seems to be colophony (Echard, 2010). Several written sources such as royal tablets and almanacs of commerce or directories of merchants and account books of bankrupt merchants (1695-1791) in the Archives of Paris²⁰ provide evidence that Parisian druggists (the corporation of *droguistes-épiciers*) sold varnishes and turpentine.

Color sellers or *vendecolori*

Color sellers appear at the end of the 15th c. in Venice under the name of *vendecolori*, and most likely originated among apothecaries. According to early inventories, these stores provided raw materials for varnishes and also ready-to-use varnishes for artisans, such as musical instrument makers and painters, showing an earlier permeability between the different specialties.

¹⁵ “Oekonomisch- technologische Encyclopädie, oder Allgemeines System der Stats- Stadt Haus- und Land- Wirthschaft und der Kunstgeschichte”, Krünitz, Korth, vol. 182, Berlin, 1844, pp.103-104 (under the term “Terpentin”)

¹⁶ “A treatise on foreign vegetables containing an Account of such as are now commonly used in the practice of Physick with their Descriptions, chemical Analysis, Virtues, Doses, and various Effects. Chiefly taken from Materia Medica of Steph. Fran. Geoffroy, M.D.”, Geoffroy, Thicknesse, 1749, J. Clarke, C. Davis, J. Wiston, S. Baker, London, p.236

¹⁷ “Der aufrichtige Materialist und Specerey-Händler oder Haupt- und allgemeine Beschreibung derer Specereyen und Materialien”, Pomet, 1717, Leipzig, Gleditsch and Weidmann, pp.423-424.

¹⁸ “Oekonomische Encyclopädie, oder allgemeines System der Land- Haus- und Staats-Wirthschaft in alphabetischer Ordnung”, Krünitz, vol. 1, Joachim Pauli, Berlin, 1773, p.80 (under the term “Terpentin”)

¹⁹ *verfverkoper(s)* in actual Dutch

²⁰ For example, Dumas and Lepée’s account book, Parisian *droguistes-épiciers*, (1782-184, Archives de Paris D5B6 349) mentions the sale of Venice turpentine used for easel paintings and a cheap turpentine that could be easily used for carriage coatings named *térébenthine pise* in French (Encyclopédie Méthodique 1783, an extension of the Encyclopédie Diderot).

Matthew (2007) mentions that, in 1502, Lorenzo da Pavia chose a varnish from a *vendecolori* for Mantegna, a painter who was satisfied with it and asked for it again¹.

- Historical documentation is available on the main locations of pine resin centers in 18th c. France, established particularly in the south-western France.
- Violin makers could get raw materials to make varnish from color sellers or apothecaries or they bought ready-to-use-varnishes directly from merchants.

3.4.2. Practices of production and storage

The mode of production of pine colophony and varnishes can have an impact on the provenance study of materials as exogenous contaminations may occur at each step of the manufacturing process. By comparing the contemporaneity of the raw materials used in varnishes with the making period of the musical instruments, storage practices are also related to the issue of the dating of materials. A few clues in written sources concern artisanal storage practices of varnishes and their ingredients in earlier violin workshops.

3.4.2.1. Harvesting and distillation of pine resins

Steigenberger (2013) reported written sources mentioning the harvesting modes of pine resin. Resin workers climbed up conifers, cut sapwood after removing the bark, and collected resin in cornets, or they removed the bark along a vertical incision made in the trunk, from the ground to a few meters high and collected the resin in containers at the foot of the tree or in trenches/holes dug in the ground^{21,22}. Pine resin was filtered through wicker baskets to remove impurities²³.

Pine resin contains a solid fraction (colophony) and a volatile fraction (turpentine). Colophony is obtained as a by-product of turpentine production. Aufan and Thierry (1990) reported various processes to produce turpentine based on written sources²⁴ in the 18th c.: i- by baking in ovens without a still, ii- by a natural distillation process using the heat of the sun especially at Teste de Buch, iii- by boiling over a fire and distillation in a still. Steigenberger (2013) also reported the natural distillation of pine resin placed in perforated wooden containers with turpentine gradually flowing through the holes. Another example cited is a wooden barrel containing turpentine placed in a brick furnace, fluidized, then filtered through straw and bottled²⁵. Turpentine was exported in wooden barrels toward other European countries such as Holland and England.

Distillation is a mode of production used to separate turpentine from colophony with the temperature reaching the boiling point of turpentine (150-180°C). The process has been used since antiquity and was further developed in 16th-c. Europe (Mills and White, 1987). However, distilled colophony was essentially produced on a limited scale in (al)chemical experiments or medical recipes. The most common colophony sold by apothecaries and druggists was simply raw resin, possibly filtered, that had been cured. The commercialized turpentine and colophony

²¹ Krünitz 1773, p.80 (under the term “Terpentin”) (see note 18)

²² “A history of the Material Medica”, Hill, 1751, T. Longman, C. Hitch and L. Hawes, A. Millar, J. and J. Rivington, London, p.710

²³ “An experimental history of the materia medica, or of the natural and artificial substances made use of in medicine”, Lewis, 1761, H. Baldwin, London, p.552

²⁴ as reported by the Abbé Desbiey in the 18th c.

²⁵ Krünitz 1844, p.103-104 (under the term “Terpentin”) (see note 15)

resulting from distillation were mentioned apparently without any particular modifications or additions¹.

The development of distillation essentially depends on developments in laboratory distillation tools. In the 16th c., methods of direct heating, water bath and sand/ash bath were used, as well as metal boilers and stills, mainly made of copper. However, the metal equipment was subject to corrosion. There were minor changes in the equipment until the 18th c. with the use of glass, sandstone and ceramic stills and new standard shapes were tested. The apothecary-chemist Von Löwenstern was one of the first to prefer glass equipment in the early 18th c. (Krell, 1982; Kockmann, 2014).

The industrial production of turpentine and colophony in distilleries really developed from the 18th c. onwards. In his Treatise on forestry, Duhamel du Monceau mentioned the cooking of pine resins from firs and pines in copper boilers on brick furnaces²⁶. Guy de Coincy (1936) mentioned that, from the mid-18th c., distillation workshops were placed in the vicinity of forests and equipped with boilers. Nevertheless, the methods of preparation by cooking or distillation existed simultaneously despite the development of industrial distillation. Cooking methods were likely less expensive, more widespread and easier to implement¹.

3.4.2.2. Preparation of violin colophony and varnishes

For both easel paintings and violin making, the development of distillation techniques in the 18th c. might be related to a trend towards the increasing use of alcohol solvents and alcohol-based varnishes. Indeed, a sufficiently high alcohol content must be reached to dissolve shellac and vegetal resins (Perego, 2006; Echard, 2010a). The common use by luthiers of spirits of wine enriched in ethanol and produced from grain is attested in Dresden in the late 18th c. (Meyer, 2006). When artisans chose to make their own varnishes, open fires for the preparation were particularly dangerous involving alcohols or oils with resins, causing dreadful accidents in the past. Varnishes were preferably prepared outdoors or even outside cities: "in Paris we are not very comfortable for that, we should have a yard or a garden"²⁷ (Pique to Lupot in 1792); "Many rules forbid the making of oil varnishes within cities. This policy is for safety: the materials are highly inflammable and can cause big fires"²⁸ (Watin, 1773a).

Duhamel du Monceau reported that colophony could be melted in boiling water to remove the impurities and liquid colophony was filtered in canvas bags in the late 18thc²⁹. Filtering techniques were also applied on varnishes to remove dust particles during the 18th c. using silk canvas or linen cloths, then the containers were covered to protect the varnish from dust³⁰

²⁶ « Traité des arbres et arbustes qui se cultivent en France en pleine terre », Duhamel du Monceau, 1755, Paris, H.L. Gerin et L.F. Delatour, 1755, 2 vols, pp.148-149, under the term « pin ».

²⁷ « Les facteurs d'instruments de musique, les luthiers et la facture instrumentale », Constant Pierre, 1893, p. 128-129. "à Paris on n'est pas trop commodément pour cela, il faudrait avoir une cour ou un jardin." Letter from the violin maker Pique (Paris) to Lupot (Orléans) in 1792.

²⁸ "Il est défendu par beaucoup de réglemens de faire des Vernis gras dan l'intérieur des Villes. Cette police est prudente ; les matières sont si combustibles qu'elles pourroient causer les plus grands Incendies ; d'ailleurs, elles sont si pénétrantes que l'odeur s'en porte très-loin : aussi les Vernisseurs sont-ils obligés de les faire faire hors les barriers & dans la campagne." Watin, L'art De Faire Et D'employer Le Vernis Ou L'art Du Vernisseur, Auquel on a Joint Ceux Du Peintre Et Du Doreur.

²⁹ Duhamel du Monceau, 1755, regarding « la poix grasse » (see note 25)

³⁰ Watin, 1773, p.226. « Quand le vernis est fait, il faut avoir grand soin de le purifier, le plus qu'il est possible de toute ordure & poussière, en le passant par un tamis de soie ou linge en lin ; et lorsqu'il est bien purifié, ayez la précaution de couvrir le vase qui le contient, de crainte qu'il ne tombe quelques grains de poussière dedans. »

(Watin, 1773). Filtering varnishes in cloths to remove dust might have been a widespread practice as the technique was used in China as reported by d'Incarville and as being part of the process to produce Chinese black lacquer³¹ (Watin, 1773b).

Several types of containers were used to cure varnishes. An example from Italian recipes mentioned that colophony was cured in new varnished pots³². Another recipe from 1791 indicated that the varnish was cured in a glass bottle³³.

3.4.2.3. Storage of varnishes for musical instruments

Artisans could buy their own ingredients for varnishes from stores; however, little is known regarding the storage time of varnishes and natural resins since they are consumables. Most of their use would have to be relatively immediate, or a large batch of varnish would have to be made from time to time. Devergne (1993) reported a description of carriage workshops including the production of varnishes, then kept in tin cans. The letter from the violin maker Pique to Lupot in 1792 mentioned that a previous preparation of varnish had been used for 4 years³⁴. An early recipe from 1791 mentioned that the varnish prepared could be stored in a glass bottle for a year²³.

- The resin is harvested from pine trees and collected in containers or holes made in the ground at the foot of the tree.
- The pine resin, colophony and varnishes were cleaned, cured and filtered through wicker baskets, canvas bags, or cloths to remove bark and dust particles.
- The colophony was separated from turpentine by decantation under the sun, by curing or by distillation using metal, ceramic, sandstone or glass tools.
- Violin makers could produce their varnishes in batches that could then be stored for 1 or 4 years in tin cans, glass bottles, and new varnished pots to avoid dust contamination.

4. Other materials

4.1. Strings

Research on the making of early gut strings is available in written sources (Dugot, 1983; Peruffo, 1993, 1997; Houssay, 2004; Ceulemans, 2008) and has already been used for faithful reconstructions of strings in historically informed performances, despite the lack of information

³¹ Watin, 1773, p.319. « Passer le vernis pour le purifier le plus qu'il est possible de toute ordure & poussière (...) on enveloppe le vernis comme on a fait aux autres expressions avec le coton & on l'exprime : le vernis ainsi passé est censé très pur. »

³² Galeazzi, 1791. Elementi teorico-pratici di Musica con un saggio sopra l'Arte di suonare il violino.. vol. 1, nella stamperia Pilucchi Cracas, p.78, « una pentala nueva inverniciata ».

³³ « Secrets concernant les arts et métiers », par une société d'artistes, vol. 2, 1791, p. 835. "Vernis excellent. Prenez six onces d'huile de térébenthine & deux onces de térébenthine de Venice la plus claire & la plus nouvelle ; mettez le tout dans une bouteille de verre fort, que vous ferez chauffer peu-à-peu sur un réchaud, ou sur de la cendre rouge ; lorsque les matières commenceront à bouillir vous y ajouterez une demi-once ou un peu moins de mastic en poudre ; après quoi vous continuerez de faire bouillir doucement, l'espace d'un demi-quart d'heure, alors le vernis sera fait. Il se garde un an sans se gâter."

³⁴ Pierre, 1893, pp. 128-129, « J'en ai fait il y a quatre ans, qui m'a servi jusqu'à ce jour; (...) vous m'obligeriez de m'envoyer cela dans une petite bouteille avec du raucourt pour mettre sous le safran. » (see note 28).

about early technological processes in the descriptions (Longhi, 2019; Lacheze and Weckerle, 2021). In the meanwhile, research through material analyses is currently limited in its efforts to write a “gut string history”. For instance, preliminary analyses reported by (Houssay, 2004) merely suggested that early gut strips were less tightly twisted industrial strings. There is still some discussion about this observation among researchers, however.

Here, I will give a brief general overview of current knowledge on gut string making despite the fact that the processes underwent controversial changes between the 16th and the 19th c. The main concerns of violin makers are always the regularity of the string diameter and the pitch of the note.

A priori, the key steps in the making of gut strings are traditionally as follows: i- natural animal gut is made from a layer of the intestine consisting mainly of collagen, i.e. a sub-mucosa (internal part) and a serosa (external part), ii- then, it is washed, treated, cut into thin strips, iii- then, reassembled and twisted, iv- and finally dried, rubbed, and sometimes varnished or oiled. The same main steps were still used for the production of animal gut strings by the last French industry Sofracob which closed in 2011³⁵. Nevertheless, string making for musical instruments has been impacted by successive changes over the centuries. For example, wound strings appeared in the second part of the 17th c. This technique involves winding a metal wire round a gut core (Peruffo, 1997). Early gut strings were produced using artisanal techniques until the early 19th c. As reported by Barbieri (2006), pre-industrial strings were produced from strips of gut first cleaned in water and treated with alkali solutions such as potash or wine. The strips acquired a twisted structure before a sulfurization step in a sulfur gas atmosphere. At the end of the production process, they were rubbed with horse hair, cloths, pumice and plant oil.

Since the beginning of the Industrial Revolution, new chemical treatments in gut string making are to be expected. For this reason, patents from the 19th c. have been studied at the Musée de la musique showing the use of chemical substitutes for traditional products. For example, there is the use of sodium percarbonate ($\text{Na}_2\text{H}_3\text{CO}$) in the patent by Louvet 1873 n° 115 664, and for rubbing, olive oil was replaced by paraffin oil dissolved in benzene and camphorated alcohol in the patent by Lutz 1901 n°314 103³⁶. From the early 19th c. onwards, the regularity of the winding and twisting operations in string making also testifies to the emergence of mechanization of the process. As a comparison, the introduction of steam machines in wire-drawing installations was estimated c.1810-1820 (Durier et al., 2019b).

Besides, it can be noted that standardization and structural modifications were applied to many early bowed instruments from the mid-18th c. onwards, especially the replacement of the neck (Boyden et al., 2001). To satisfy the demand of European society for more virtuosity and powerful sounds, strings were submitted to increasingly higher tensile strength. A few research highlights the possible link with changes in the making processes and standardization of gut strings from the early 19th c., in a comparable way to work on iron and steel piano strings during the same period (Durier et al., 2019b).

Regarding use practices of gut strings on European stringed instruments, the highest strings are usually stretched close to the breakpoint value, so their duration of use is limited to a few months or a few years depending on how the instrument is played. Lute gut strings are also changed very often. Regarding storage practices, gut strings are controversially assumed to

³⁵ Synthèse cordes fabrication, technique Sofracob. Report, S. Vaiedelich, available at the Musée de la musique.

³⁶ Brevets de cordes d'instruments de musique. Report, S. Vaiedelich, available at the Musée de la musique.

have been stored for no more than a few months before their musical use³⁷. It is worth noting that, although the transport between the place of production of the raw gut and its place of transformation may have been optimized in a similar way to cobblers' shops, which were set up close to the slaughterhouses, the reputation of the quality of Roman and Neapolitan gut strings since the 16th c. in Europe is evidence of an early long-distance trade for violin strings (Barbieri 2006).

Currently, research on early gut strings is mainly based on written sources whereas analyses using material characterization are seldom used according to my state-of-the-art. As the literature review revealed a lack of methods to date early specimens of gut strings, ¹⁴C dating was tested during this PhD.

4.2. Glues

Traditionally, bone-nerve glues named hide glues are mostly used in violin making to join wooden parts together as structural glues. (Bonizzoni et al., 2014) reported the traditional use of hide glues in violin making due to their reversibility (using moisture or heating). Caruso et al. (2007) reported the detection of animal glue with collagen proteins for the construction of an 18th c. instrument using GC-MS but without being able to distinguish between terrestrial animal and bone glues.

Fish glues can affect ¹⁴C measurements in contrast with glues extracted from animals in direct contact with the earth's atmosphere. Upstream studies combining material analyses and written sources are necessary to prevent possible ¹⁴C contamination. A priori, terrestrial animal glues were mostly used, and "fish glue" is rarely mentioned in the early varnishes listed by Vernix³⁸.

4.3. Wood

The wood trade is one of the most important for violin making, with spruce and maple as the primary species. Traditionally, the species used for the constitutive parts are: the violin back, the ribs, the bridge and the neck in maple; the fingerboard, the nut, the scroll, and peg box, pegs, tailpiece in ebony; soundpost in spruce, etc. (Bernabei et al., 2010). Today, the wood for musical instruments is the most profitable sector of the wood industry (Viala, 2018).

The dating of spruce soundboards is commonly determined through dendrochronological studies (Beuting, 2010; Topham, 2003, 2009). Dendrochronology can also be used to track the provenance of wood as reported by Grassmann (2009) for spruce from the Fribourgian pre-Alps used by a London luthier in the 18th c. However, most of the wooden parts of bowed instruments cannot be dated by means of dendrochronology. This is due to the traditionally selected wood species, such as ebony fingerboard, cherry wood pegs, maple ribs and to too short series of tree rings. An alternative for provenance studies could be the application of Sr isotope analyses on wooden parts (Bernabei, 2020), while ¹⁴C dating could be an alternative to

³⁷ Personal communications, Anne-Emmanuelle Ceulemans and Stéphane Vaiedelich.

³⁸ An anonymous varnish recipe mentioned the adding of fish glue: "Vernis pour les tailles-douces. Après avoir couché de l'eau où on a dissous de la colle de poisson, on fait un vernis avec demie livre d'esprit de vin, de gomme elemi deux gros, & sandarac trois gros, 12.pt, fait un gros." in *Secrets concernans les arts et les métiers*. Nouvelle édition, ed ; C. Ferrand, Rouen, 1724, p. 95-96.

date them (Chase et al., 2009; Durier et al., 2019a). However, storage duration and the re-use of ancient wood for violin making have to be taken into account.

Current practices regarding the drying duration of wood or the reuse of older wood cannot be considered as a reliable reference to document early practices. However, by comparing the given date of manufacture of early instruments (for example on the label), with the dating provided by dendrochronology on the most recent tree ring of the soundboard, it is possible to estimate the mean storage duration of the wood according to the historical/geographical context. For example, Bernabei et al. (2010) reported a dendrochronological study showing that the drying duration was estimated to be around ten years in the 18th c. for instruments from the collection of the Cherubini Conservatory (Florence, Italy).

A mean value of storage duration of around 20 years was estimated based on dendrochronology dating performed on instruments from the collection of the Musée de la musique (Paris) by Topham (unpublished). A value Δt for each instrument corresponds to the difference between the label date of the instrument and the most recent tree ring of the soundboard (Table 2).

Table 2. Table of dendrochronology dating performed on some instruments from the collection of the Musée de la musique (Paris) by Topham (unpublished)

Inv. no.	Instrument	Date (?)	Origin	Maker	Dendrochronology (most recent ring)	Δt (years)
E.654	violin	1669	Absam	Jacob Stainer	1607	62
E.1375	violin longuet	1699	Cremona	A. Stradivari	1682	17
E.1111	Violin "Davidoff"	1708	Cremona	A. Stradivari	1697	11
E.1932	violin "Tua"	1708	Cremona	A. Stradivari	1698	10
E.1730	violin "Provigny"	1716	Cremona	A. Stradivari	1699	17
E.1729	violin "Sarasate"	1724	Cremona	A. Stradivari	1713	11
E.983.1.8	violin	1730	Rome	Francesco Emiliani	1704	26
E.983.1.6	violin	1740	Gênes	Bernardo Calcagni	1725	18
E.1217	violin "Alard"	1742	Cremona	G. Guarneri del Gesu	1736	6
E.983.1.2	violin	1757	Milan	attr. P. A. Testore	1701	56
E.980.2.423	violin	1780	Paris	Jean-Nicolas Lambert	1771	9
E.983.1.14	violin	1827	Vienna	Nicolas Georg Ries	1815	13
Mean estimated storage and drying duration						20

For comparison, in Flemish easel painting, frames and supports were made of wood with a drying duration that has been evaluated at from 6 to 8 years in the 15th c. and that was reduced to 3 to 5 years at the end of the 16th c. and 17th c. (Verougstraete and Van Schoute, 1989).

¹⁴C dating might be impacted by the effect of extraction from the internal or external part of the tree, the duration of wood seasoning (*i.e.* wood cleared of its sap), storage before manufacturing, or the re-use of wood by violin makers. An early example with an extreme storage duration is the Vihuela de mano from the late 16th c. (E.0748, coll. Musée de la musique) which has its most recent ring dated from 1496 according to Topham. Examples of the impact of different wood storage or re-use practices on ¹⁴C measurements were studied for two Indian vinas and a Chinese zither (Durier et al., 2019a, 2021). Here, I tried to anticipate the issue of the impact of underlying wood on the ¹⁴C measurements of the protective varnish by diffusion between the two materials and by contamination during the sampling.

5. Conclusion

Glues could have been added through successive repairs and restorations. Different kinds of glue were chosen according to their properties and are still currently used by restorers following traditional practices including fish glue (Schellmann, 2007). From the 20th c. onwards, synthetic water-based vinyl glues could have been used. To avoid contamination, the distribution of glue on the violin surface can be detected by combining UV light and FT-IR (Invernizzi et al., 2018).

Based on the state of the art of European varnishes, the constitution of a material corpus of early varnishes focused mainly on linseed oil-colophony varnishes applied on stringed musical instruments, furniture and sleds from the late 17th c. to the early 18th c. for several reasons:

- The calibration curves lead to more reliable values in the following range of dates during the modern period: [1600 - 1730] or [1770 - 1810].
- The original varnish layers were traditionally preserved on these Heritage objects which are also objects of use with traces of their material history in the successive varnish layers
- The composition of linseed oil/colophony varnishes in violin making has been widely studied in the literature (Bucur, 2016). “Martin varnishes” contained oil/colophony in the early 18th c. and were used on musical instruments, furniture or carriages. Linseed-oil/colophony varnishes were used prior to oil/copal varnishes which came into use c.1730-50 for their weathering-resistance on carriages, and oil/colophony mixtures were preferentially used for gilding decors in the early 18th c.

The issues related to the early mode of production, trade and storage of organic binders are linked with the dating and provenance studies using ¹⁴C geochronology and isotope geochemistry analyses. Concerning the colophony studied in this PhD, the main historical pine resin centers in 18th c. France were located in southern France including the Landes. The resin was harvested and collected in containers or holes in the ground. The colophony/turpentine separation was generally done by curing, but also possibly by decantation under the sun or by distillation with mainly copper or glass tools. Pine resin, colophony and varnishes were successively cleaned, heated and filtered through wicker baskets, canvas bags, and cloths to remove contaminants (bark, dust, etc.). The trade in raw organic binders (to make varnish) and ready-to-use-varnishes was mainly carried out by color sellers or apothecaries. Varnishes could be produced in batches that lasted for 1 to 4 years if stored in tin cans, glass bottles, or new varnished pots to avoid dust contamination.

CHAPTER 2. Chemical characterization of natural resins and of colophony/linseed oil varnishes

1. Introduction

This chapter reviews current knowledge on the chemical characterization of colophony and other natural resins commonly used in oil-based varnishes for violin making. It focusses on the characterization of colophony/linseed oil varnishes from the preparation of the mixture with raw ingredients to the oxidation of the dried film. The chemical approach developed here is another tool that helps to apprehend dating and provenance studies of organic binders and early varnishes of the modern period (from the 16th c. to the 19th c.). This approach provides clues to the historical approach through written sources (and vice versa).

Previous reviews on the organic composition of natural resins, their botanical/geographical origins and their historical periods of use in Europe are abundant in the literature (Burger, 2008; Daher, 2012; Azémard, 2014; Tirat, 2015; Decq et al., 2021). The botanical families of natural resins and their main geographical provenances are briefly summarized in Table 3 and Figure 27 (Mills and White, 1987). More details are provided in Figure 27. Studies have reported that the detection of biomarkers in natural resins can be related to taxonomic characterization and species distribution on a territory (Regert et al., 2008; Le Milbeau et al., 2013). The detection of stable isotopes and multi-elements are also indicators of geographical traceability (Liu et al., 2019). However, Sr isotopy was finally selected and tested to trace the origin of organic binders during this PhD, following the state-of-the-art presented in this chapter that explores the main organic chemical components and inorganic elements at major, minor and trace levels.

Table 3. Species and their main geographical provenances involved in the production of natural resins in violin making.

Plant resins	Botanical family (see Figure 27)	Provenance
Colophony	Pinaceae	Europe, Asia, Africa, America
Sandarac	Cupressaceae	Mediterranean coasts, North Africa, Australia
Chios mastic	Anacardiaceae	Mediterranean coasts
Dammar gum	Dipterocarpaceae	India, East Asia
Benzoin	Styracaceae	Southeast Asia
Copal (subfossil)	Fabaceae	Africa, Brazil, South America
Baltic amber (fossil)	Different paleobotanical sources	East Russia, Poland, Lithuania
Animal resins	Species	Provenance
Shellac	Insect Coccoidea	India, China

After reviewing natural resins, chemical characterization is used to apprehend the complex chemical composition of early oil/colophony varnishes for the application tests of ^{14}C geochronology and geochemistry analyses.

This chapter is divided into three parts including a short review of: i- the current definition, the geographical/botanical origins and the history of use of colophony in Europe, ii- its organic molecular characterization, iii- the elemental composition of colophony (part 1), a similar review on current knowledge of natural resins in early varnishes for instrument making (part 2), the description of the chemical characterization of linseed oil/colophony varnishes used in violin making and horse-drawn carriages, including the organic compounds, the linseed oil/colophony mixture, the film ageing, and the driers and pigments (part 3).

2. Colophony

2.1. Definition, origin and use

Conifers from the Pinaceae family exude an oleoresin to protect themselves against external aggressive factors (wind, wounds inflicted by insect attacks, etc.). For varnish production, this resin is collected by tree tapping, and the solid fraction named colophony is separated from the volatile fraction named turpentine by distillation. The resin is extracted from a large range of pine species in Europe, the United States, Asia, Africa, South America (*P. pinaster*, *P. elliottii*, *P. kesiya*, *P. yunnanensis*, *P. massoniana*, *P. sylvestris*, *P. alepensis*, etc.) (Langenheim, 2003) (Tables 1 and Figure 27).

The solid fraction of pine resin named colophony was traded since Antiquity in Europe for its waterproofing and adhesive properties (André, 1964; Aufan and Thierry, 1990) – and earlier (Rageot et al., 2019). For example, it was used for caulking ancient boats, for varnish making or to adjust the friction of strings of musical instruments. Colophony has the advantage of being a cheap resin that could be used in large amounts for varnish making. However, oil/colophony varnishes have the drawback of drying slowly (taking several weeks or months) as well as breaking and darkening over time. Since the early 18th c., early recipes of alcohol-based varnishes became progressively more abundant than those of oil-based varnishes (Echard and Malecki, 2012), whereas the use of oil-based varnishes persisted longer for carriage coatings as they have a better resistance to weathering (Augerson, 2011) ([Chapter 1 - § 3.3.3](#)).

The volatile fraction of resins from other Pinaceae species, named turpentine, was also used for the making of early varnishes especially as a diluent. Turpentine was also extracted from fir (*Abies alba*, *Abies balsamea*) and from spruce (*Picea abies*). Venice turpentine extracted from larch (*Larix decidua*) is an undistilled oleoresin which has a different chemical composition (with specific neutral labdanes) compared to turpentine extracted from pines, firs and spruces, but was also quite renowned as a diluent in varnish making (Langenheim, 2003; Azémard, 2014).

2.2. Organic geochemistry: molecular characterization

Colophony is a diterpenoid resin. Diterpenes ($\text{C}_{20}\text{H}_{32}$) belong to the terpene class which is a group of organic molecules produced by plants composed of 2 isoprene units C_5H_8 . Strictly

defined, diterpenes comprise four isoprenes i.e. (C₅H₈)₄. Colophony contains molecules with a diterpene skeleton from two groups of carboxylic acids, abietanes and pimaranes (Figure 10):

- Abietanes: (mostly) abietic, neoabietic and palustritic acids
- Pimaranes: (mostly) pimaric acids, isopimaric and sandaracopimaric acids

The most abundant molecule is dehydroabietic acid (DHA) (Mills and White, 1987; Tirat, 2015).

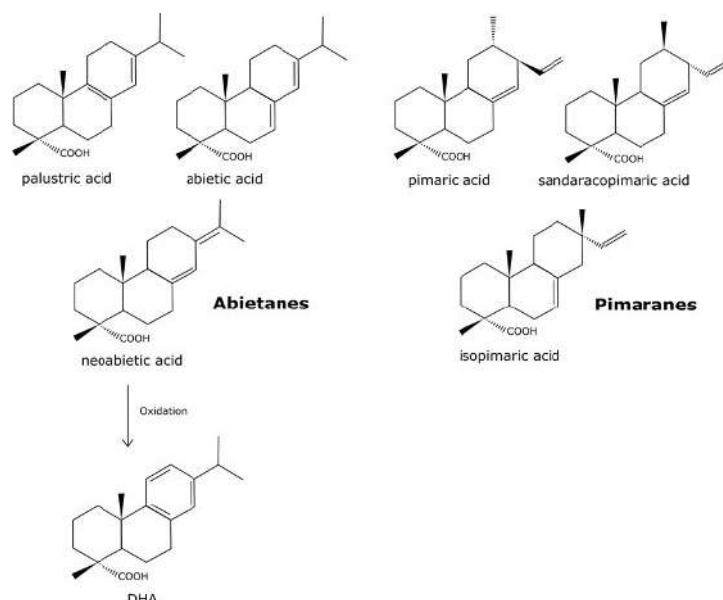


Figure 10. Abietane and pimarane diterpenoid acids, the most abundant molecules in colophony (adapted from Tirat, 2015)

2.3. Mineral geochemistry: elemental analysis

We compared the chemical element content of colophony found in the literature as a possible source of information on geographical origin. Zhang et al. (2013) reported multi-element analyses using ICP-OES on Chinese colophony (China being the largest actual supplier). Table 4 indicates that Sr concentration is less than 1 ppm.

Table 4. Multi-element analyses on Chinese colophony. Mass concentration in ppm reported by Zhang et al. (2013)

	Al	As	B	Ba	Bi	Ca	Cd	Co	Cr	Cu	Fe	K
<i>Pinus elliotti</i>	8.7	0.4	0	0.3	1.2	166.0	0.2	0	0.1	0	7.7	16.7
<i>Pinus kesiya</i>	38.9	0.4	0	0.2	0.7	64.6	0.1	0	0.2	0	10.5	9.1
<i>Pinus yunnanensis</i>	25.5	0	7.4	0	0.9	0	0	0	0	1.9	0	0.9
<i>Pinus massoniana</i>	238.0	0	5.5	0	0.3	0	0	0	0.3	0.6	9.0	0.5
	Li	Mg	Mn	Na	Ni	P	Pb	Se	Sr	V	Zn	
<i>Pinus elliotti</i>	0	31.5	0.2	51.4	0.7	0	1.5	5.3	0.9	0.3	3.9	
<i>Pinus kesiya</i>	0	11.4	0.1	17.1	0	0	0.8	5.2	0.4	0.3	1.0	
<i>Pinus yunnanensis</i>	0.2	0	0	0	0.1	0	2.6	4.6	0	0.1	0.4	
<i>Pinus massoniana</i>	0.1	56.8	0.7	0	0.9	1.8	2.0	2.0	0	0	4.2	

3. Other natural resins

3.1. Sandarac

3.1.1. Definition, origin and use

Sandarac commonly exudes from cypress trees belonging to the Cupressaceae family (Mills and White, 1987; Scalarone et al., 2002). It is soluble in alcohol and has a melting point around 150°C. Today, sandarac is a commercial name of the *Tetraclinis articulata* resin, extracted by resin tapping and by collecting exudations that follow natural injuries. The species is distributed in North African countries such as Morocco, Algeria, Tunisia and other Mediterranean regions such as South-Eastern Spain (between Cartagena and Malmeria) and Malta. The Atlas region of Morocco is still a major supply area. The port of Mogador (the present-day city of Essaouira) was a historical centre for the export of sandarac, mainly to Europe (Langenheim, 2003). Musselman (2007, p280) reported that the collection of sandarac was forbidden by the authorities in the mid-20th c., and is still restricted today (El Mouridi, 2011). Williams (2011) indicated a shortage in African sandarac during this period, leading to the exportation of Australian sandarac mainly from *Callistris* resin (Murray River), a substitute with a similar composition and commercial name, which had so far been used by the local population.

Historically, African sandarac from *Tetraclinis articulata* has been used. However, some confusion occurred in the past with *Juniperus* resins that also came from Mediterranean regions, maybe due to very similar botanical origins (Cupressaceae) (Mills and White, 1987; Azémard et al., 2017). There is still confusion today about the botanical identification of tree resins sold as sandarac (Decq et al., 2021).

Sandarac has been traded since Antiquity as well as mastic gum (Musselman, 2007, p280). The resin has also been used since the Middle Ages for both alcohol and oil-based varnishes (Azémard et al., 2017). Manuscripts mentioned “vernice liquida” as an early high quality and famous Italian varnish made of linseed oil and sandarac (Merrifield, 1849). It was used by painters such as Leonardo Da Vinci but also applied on wooden artefacts (Kononenko, 2017). Azémard et al. (2017) mentioned that sandarac lost its popularity in varnish making with the appearance of turpentine spirit varnishes at the end of the 18th c. and dammar varnishes during the 19th c., while it was still used on wood (especially in violin making). However, we cannot refer to an available database of early recipes of varnishes such as Vernix to statistically support this assumption³⁹. Schröter et al. (2019) found sandarac among the ingredients of varnish recipes dated from 1803 to 1893.

3.1.2. Organic geochemistry: molecular characterization

The natural resin named sandarac is currently defined as a diterpenoid resin (with 4 isoprene units or 20 carbons) mainly comprising labdanes, i.e. bicyclic molecules with an unsaturated side-chain of 6 carbons, in particular highly polymerised polycommunic and communic acids with communal molecules (Figure 11).

³⁹ Only one early recipe of varnish from the 19th c. is listed in the Vernix database.

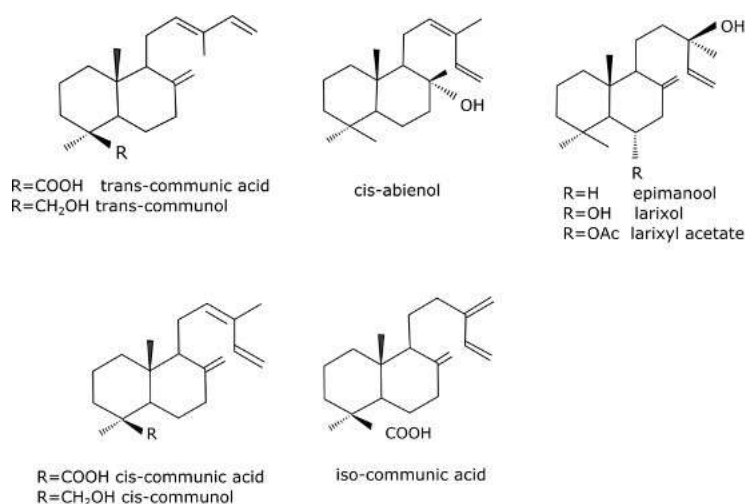


Figure 11. Communic acids, i.e. diterpenes with labdane skeletons, the most abundant molecules in sandarac (Mills and White, 1987).

3.1.3. Mineral geochemistry: elemental analysis

Elemental analyses using ICP-AES can be found in the literature for *Tetraclinis articulata* leaf (Achak et al., 2009). Unfortunately, the Sr concentration is not mentioned (Table 5). To our knowledge, elemental analyses including Sr have not been reported on sandarac resins.

Table 5. Multi-element analyses on *Tetraclinis articulata* resin, Marrakech region. Mass concentration in ppm (Achak et al., 2009).

	Al	Ca	Fe	Cu	Fe	Zn	Mg	S	Si
<i>Tetraclinis articulata</i>	7	487	8	6	8	3	35	20	18

3.2. Mastic gum

3.2.1. Definition, origin and use

Mastic is a natural resin collected by tree tapping from a Mediterranean shrub named *Pistacia lentiscus* belonging to the Anacardiaceae family. The *Pistacia lentiscus* grows under the Mediterranean climate across several countries such as Portugal, Spain, southern France, Morocco, Tunisia, Greece, Syria, Israel, Iraq, Eastern Iran and Turkey (Langenheim, 2003) (Table 48). The resin from Chios Island had the highest reputation and has been abundantly documented. Its traditional production was classified as an Intangible Cultural Heritage by UNESCO in 2014.

Mastic has been traded especially to Egypt since Antiquity. It was renowned in Antiquity for curing wounds and disinfecting (Musselman, 2007, p269). Mastic-based varnishes have been used on wood and paintings at least since the Middle Ages in Europe. Dammar became an interesting substitute during the 19th c. (Azémard et al., 2017).

3.2.2. Organic geochemistry: molecular characterization

Mastic is a triterpenoid resin in which the main chemical compounds are masticadienonic acids from the euphane group of tetracyclic triterpenes, oleanonic and moronic acids from the oleanane group of pentacyclic triterpenes (Daher, 2012) (Figure 12).

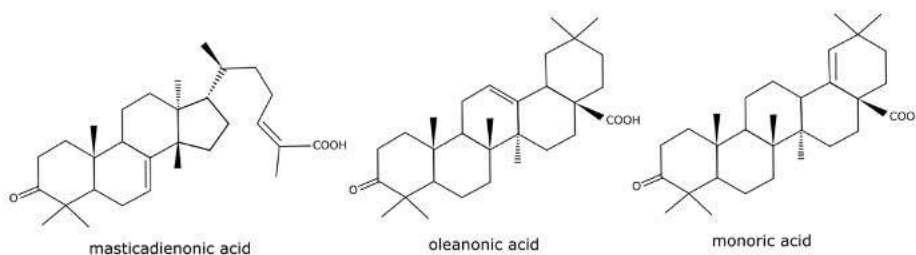


Figure 12. Masticadienonic, oleanonic and moronic triterpenoid acids, the most abundant molecules in mastic gum (Daher, 2012).

3.2.3. Mineral geochemistry: elemental analysis

Rousis et al. (2014) reported an elemental analysis of mastic gum from Chios with around 0.5 ppm of Sr (Table 6).

Table 6. Multi-element analyses on mastic gum from Chios. Mass concentration in ppm (Rousis et al. 2014).

	Na	Mg	Al	K	Ca	Ti	V	Mn	As	Fe	Co	Ni
Chios mastic	19.4	167.4	23.72	12.46	0.294×10 ³	2.47	0.133	0.406	0.0825	20.1	0.01452	0.2133
	Cu	Zn	Se	Sr	Nb	Ag	Cd	Cs	Ba	Hg	Pb	
Chios mastic	0.471	1.77	0.0109	0.480	4.33×10 ⁻³	4.92×10 ⁻³	0.0173	8.12×10 ⁻³	0.3703	8.74×10 ⁻³	0.2979	

3.3. Dammar gum

3.3.1. Definition, origin and use

Dammar is a terpenoid resin like mastic gum and exudes from trees of the Dipterocarpaceae family growing in India and Southeast Asia (Sri Lanka, Myanmar, and Malaysia) (Table 48). *Shorea robusta* is one of the most representative species producing this resin in India. Dammar gum has been used in varnish since the 19th c. in Europe (Langenheim, 2003).

3.3.2. Organic geochemistry: molecular characterization

Dammar comprises mainly dammarenolic acids from the dammarane group of tetracyclic triterpenes and ursonic acids from the ursane group of pentacyclic triterpenes (Mills and White, 1987; Daher, 2012) (

Figure 13).

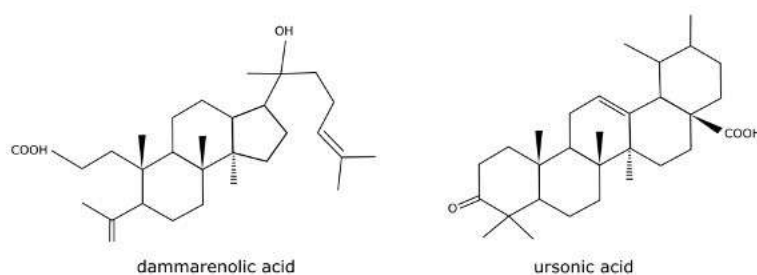


Figure 13. Dammarenolic and ursonic acids, the most abundant molecules in dammar resin (Mills and White, 1987).

3.3.3. Mineral geochemistry: elemental analysis

Breulmann et al. (1998) reported a Sr content around 15 ppm in leaves, 33 ppm in twigs and 8 ppm in trunks of trees from the Dipterocarpaceae family (Table 7). The values reported here highlight the variations of inorganic chemical content in the different organs of the trees. To our knowledge, elemental analyses comprising Sr have not been reported on dammar resins.

Table 7. Multi-element analyses on leaves, twigs and trunks of trees from the Dipterocarpaceae family. Mass concentration in ppm except for N, K, Mg and Ca in % (Breulmann et al., 1998)

	N	Si	Co	Cr	Cu	Fe	Mn	Mo	Ni	V	Zn	Li	Na	K	Rb	Cs
Leaves	1.41	217.33	0.31	0.47	5.96	38.44	204.04	0.00968	3.26	0.01914	11.44	0.11	67.64	0.92	13.06	0.11
Twigs	0.72	88.91	0.45	0.27	10.56	21.77	217.73	0.00910	2.96	0.01777	24.74	0.06	194.37	0.73	11.99	0.15
Trunks	0.24	60.85	0.07	0.53	1.83	12.14	23.09	0.01936	0.28	0.01198	7.40	0.02	34.27	0.23	3.31	0.06
	Mg	Ca	Sr	Ba	B	Al	Ga	In	Tl	Sn	Pb	As	Sb	Bi	I	Y
Leaves	0.17	0.30	15.13	17.18	18.82	22.38	0.04	0.00017	0.00249	0.03652	0.33	0.10802	0.00022	0.00119	0.17	0.00892
Twigs	0.18	0.49	32.50	29.16	11.46	17.79	0.02	0.00004	0.01134	0.03237	0.48	0.01950	0.00003	0.00117	0.23	0.00864
Trunks	0.03	0.11	7.75	12.69	2.81	11.09	0.01	0.00014	0.04629	0.02528	0.66	0.03054	0.00106	0.00091	0.04	0.00191
	La	Ce	Pr	Nd	Eu	Tb	Th	U	Ti	Zr	Nb					
Leaves	0.00501	0.13953	0.00109	0.00276	0.00056	0.00009	0.00260	0.00124	2.02	0.00524	0.00030					
Twigs	0.00615	0.01357	0.00144	0.00287	0.00127	0.00010	0.00099	0.00125	1.96	0.00053	0.00036					
Trunks	0.00425	0.00348	0.00060	0.00009	0.00015	0.00007	0.00079	0.00345	0.31	0.00817	0.00107					

3.4. Benzoin

3.4.1. Definition, origin and use

Benzoin is an Asian phenolic resin which is exuded by tree tapping from *Styrax* of the Styracaceae family with a major production in Southeast Asia (Sumatra, Java, Laos, Thailand) (Table 48). There are two main sources: i- Siam styrax which is from *Styrax tonkinensis* and *Styrax benzoides*, and ii- Sumatra styrax from *Styrax benzoin* and *Styrax paralleloneurum* (Langenheim, 2003; Burger et al., 2016). Benzoin was introduced into alcohol-based varnishes in the mid-16th c. in Europe (Merrifield, 1967). It is employed for the maintenance of the varnishes of stringed instruments (Échard, 2010).

3.4.2. Organic geochemistry: molecular characterization

Benzoin comprises benzoic and cinnamic acids, classified as carboxylic acids and deriving from the benzene and styrene groups, as well as their ester such as coniferyl benzoate and some triterpenes (Mills and White, 1987; Langenheim, 2003; Burger et al., 2016) (Figure 14).



Figure 14. Benzoic and cinnamic acids, the most abundant molecules in benzoin resin (Mills and White, 1987).

3.4.3. Mineral geochemistry: elemental analysis

Based on samples from numerous trees including *Styrax paralleloneurum* in Sumatra tropical forest, Masunaga et al. (1998) reported variations in chemical element content according to tree species and their organs, as well as Sr content in leaves and barks (Table 8). To our knowledge, elemental analyses comprising Sr have not been reported on benzoin resins and studies specifically on *Styrax* trees are scarce (Masunaga et al., 1997).

Table 8. Multi-element analyses on leaves and bark from tropical trees in West Sumatra, Indonesia. Mass concentration in % and ppm (Masunaga et al. 1998)

	S	K	Al	Ca	Mg	Cl	Si	Na	B	Cu	Fe	Mn	P	Sr	Zn	
	%							ppm								
Leaves	2.78	9.44	2.04	16.9	2.62	-	6.94	147	-	9.8	156	532	1,003	29.5	19.2	
Bark	1.44	4.10	2.01	26.9	1.16	1.24	0.80	168	9.3	9.7	120	301	139	65.9	17.1	

3.5. Copal

3.5.1. Definition, origin and use

Copals are classified in two groups: Leguminosae (or Fabaceae) and Araucariaceae resins (Langenheim, 2003). “Copal” is a controversial term broadly used today for a hard resin that is softer than amber with a high but lower degree of polymerization. The age of this resin is also controversial as copals can be subfossil resins aged between 5,000 and 40,000 years harvested from soils and riverbeds, or fresh resins extracted by tree tapping (Langenheim, 2003).

- Leguminous copal

Leguminous copal is a diterpenoid resin produced by trees belonging to the Leguminosae or Fabaceae family. The subfossil or fresh resin is produced by a large range of different botanical species from the *Hymenaea*, *Guibourtia*, *Daniellia*, *Copaifera*, *Trachylobium*, *Bureraceae* genus growing in the tropical forests of East Africa (Congo, Sierra Leone, Zanzibar), Madagascar, Central America (Mexico, Brazil) or West India (Table 48). Like amber, the botanical composition of subfossil copal is complex and has varied over geological time (Langenheim, 2003; McCoy et al., 2017).

Leonard et al. (2001) reported that copal was known by 17th c. painters, but surviving original layers of varnish to attest it are scarce. Langenheim (2003, p.397) briefly mentioned that an African copal trade formerly existed between Arab and Indian traders before a development by the Portuguese in the late 18th c. Since the mid-18th c., copal has been widely used in varnishes for furniture and carriages (Watin, 1773a; Mayer, 1976)(Chapter 1 – § 3.3.3).

According to Augerson (2011), European carriage makers imported (fresh or subfossil) American copal in the 18th c., and African copal since around 1830.

- Araucarian copals

Araucarian copals, Manila copal and Kauri copals, are a diterpenoid resin produced by trees belonging to the Araucariaceae family and are both from the *Agathis* species. Manila copal gets its name from a port in the Philippines that was a major supplier as well as Indonesia and New Zealand. Kauri resin is present in New Zealand, Australia and East India and was mainly supplied by New Zealand during the 19th c. for the making of European varnishes (Langenheim, 2003). For example, European carriage makers used kauri copal introduced in the 19th c. (Augerson, 2011).

3.5.2. Organic geochemistry: molecular characterization

Leguminous copals are made of a macromolecular structure of molecules with a labdane skeleton. They comprise mainly polymerized communic acids, and other labdanes (C₂₀H₃₈) such as ozic, eperuic, copalic, guamaic, oliveric and daniellic acids (Mills and White, 1987) (Figure 15).

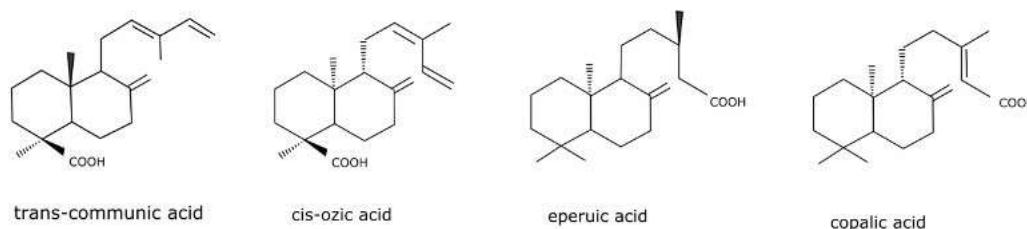


Figure 15. Communic, ozic, eperuic, copalic acids, the most abundant molecules in Leguminous copal resin (Fabaceae family) (Mills and White, 1987).

Araucarian copals comprise mainly communic acids, and other labdanes (C₂₀H₃₈) such as sandaracopimaric and agathic acids. Their chemical composition is close to that of sandarac (Mills and White, 1987)(Figure 16).

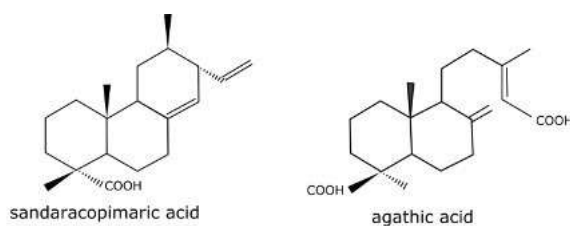


Figure 16. Sandaracopimaric and agathic acids, the most abundant molecules in Araucarian copal resin (Mills and White, 1987).

3.6. Amber

3.6.1. Definition, origin and use

Amber is a fossil resin that is harder than subfossil copal and with a higher degree of polymerization. Radiocarbon dating can be applied to detect the presence of fossil (>40000 years) or subfossil resins (5000-40000 years) due to their geological ages (Anderson, 1997). Anderson (1992) defined fossil resins or resinites as solid organic macro or micro particles found in coals and other sediments deriving by diagenesis from the resins of higher plants.

Based on chemical structural characterization, resinites are classified into four classes: class I resinites divided into the sub-classes a, b and c (including a sub-class Id reported by (Poulin and Helwig, 2012), class II, III and IV resinites; Baltic amber is listed in the sub-class Ia resinites (Anderson, 1992).

Ambers are found worldwide with different chemical structures. Here, we focus on Baltic amber which is an important geological deposit widely exploited in Europe since Antiquity (Langenheim, 2003). The paleobotanical sources of amber are controversial as the chemical composition of ambers is still ambiguous and difficult to link with botanical remains. Class I resinites have botanical affinities with Araucariaceae, Leguminosae, Pinaceae and Cupressaceae trees (Anderson, 1992). Baltic ambers are assumed to derive from Araucarian Agathis-like or pinaceous Pseudolarix-like trees from past forests (Langenheim, 2003).

The use of Baltic amber to produce amber varnish is attested since at least the 20th c. in Europe. Amber is extracted by dry distillation or melted with oil at high temperatures. The amber varnishes yielded are hard but dark and rather expensive (Mills and White, 1987; Langenheim, 2003). Baltic amber (or “succin”, “carabe”) has also been mentioned as a varnish compound in the 18th, 19th and 20th c. recipes⁴⁰ and literature based on written sources (Eastlake, 1847; Merrifield, 1849; Carlyle, 2001). (Cattersel, 2019) also reported the mention of amber in early lacquer recipes between 1620⁴¹ and 1886⁴². (Augerson, 2011) states that Baltic amber was used as a hard rubbed varnish such as copal on horse-drawn carriages. Amber has also often been described as the secret ingredient behind the quality of the oil paintings of Flemish painters such as Van Eyck. However, only linseed oil and pine resin have been detected using GC-MS (Effmann, 2006). In the same way, amber varnish has long been considered the secret ingredient of Stradivarius violins, but Echard (2010) reported the use of linseed oil/colophony varnishes through physico-chemical analyses and referred to possible ambiguities in historical terminology and botanical classification. Until now, the detection of fused amber is controversially undetectable in early varnishes due to the alteration of biomarkers (such as polycommunic acids) during heating and the complex mixture with oil (Baese, 1986; Van Keulen, 2014).

3.6.2. Organic geochemistry: molecular characterization

Amber is a fossilized diterpenoid resin composed of a highly polymerized structure of labdanes comprising mostly communic acids, and succinic acids whose link with diagenetic steps is controversial (Mills and White, 1987; Langenheim, 2003; Wolfe et al., 2009) (Figure 17).

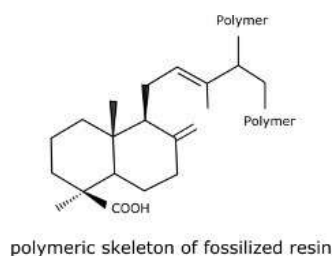


Figure 17. Highly-polymerised structure of labdanes in amber resin (adapted from Langenheim, 2003).

⁴⁰ 92 recipes out of 409 (i.e. one in five) are listed by the Vernix database under the term “ambre”.

⁴¹ De Mayerne’s treatise, 1620-1646

⁴² James Cameron’s recipe, 1886, London

3.7. Shellac

3.7.1. Definition, origin and use

Shellac is an alcohol-soluble resin produced by an insect of the family of Coccoidea, from the species *Kerria lacca* fed by its host trees. India had always been the largest producer of shellac, but it is also produced in other Asian countries such as Myanmar (Burma), Laos, Thailand and China. The most common species of host trees that feed the insects are *Butea* (Fabaceae), *Ziziphus* (Rhamnaceae), and *Schleichera* (Sapindaceae) (Langenheim, 2003).

Shellac was traded in Europe as a component of varnishes mainly through colonial India during the 17th c. The Jesuit communities in China or India helped to spread the knowledge about its harvest, properties and use (Gibson, 1942). This natural resin contains anthraquinone-based dyes, making it a cheaper red pigment than cochineal, so it was traded on a large scale in Europe from the second half of the 17th c. on (Chenciner, 2011). Shellac varnishes were detected on a large corpus of fine stringed instruments in France, Germany, Spain dated from the end of the 17th c. and the 18th c. (Échard, 2010).

3.7.2. Organic geochemistry: molecular characterization

Shellac is a resin comprising aliphatic acids, mainly aleuritic and butolic acids, with sesquiterpene derivatives such as jalaric acids ($C_{15}H_{20}O_5$) and shellolic acids ($C_{15}H_{20}O_6$). Polymerized shellac consists of chains of aliphatic acids linked to cyclic terpenes (Mills and White, 1987; Daher, 2012) (Figure 18, Figure 19).

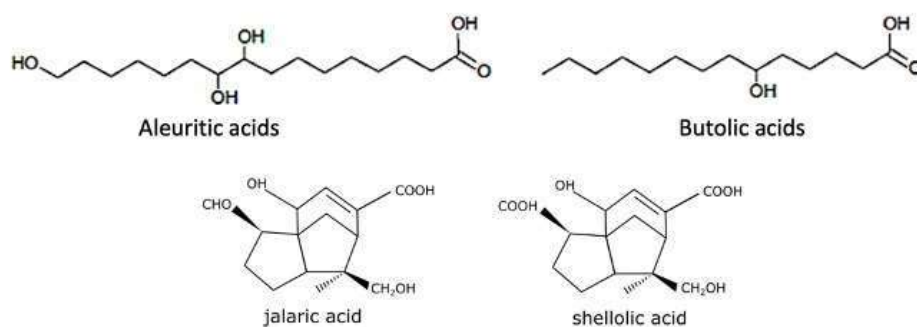


Figure 18. Molecular compounds in shellac resin (adapted from Mills and White, 1987).

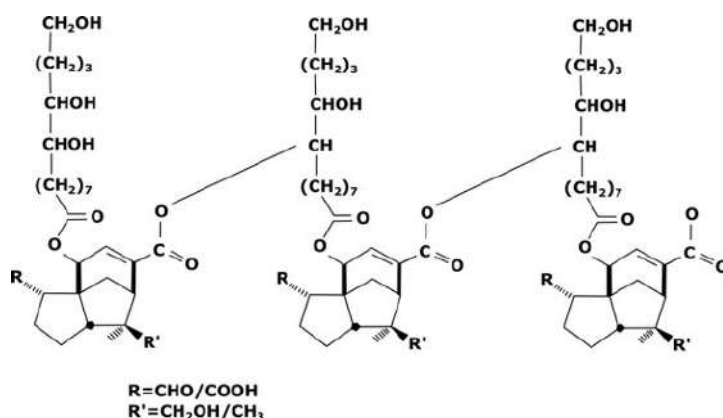


Figure 19. Polymerized aliphatic acids with sesquiterpene derivatives in shellac resin (adapted from Mills and White, 1987).

3.7.3. Mineral geochemistry: elemental analysis

Chen et al. (2005) reported that the presence of lac insects has an impact on the inorganic element content of the host trees (Table 9). Thus, we assumed that the elemental composition of shellac would be related to the mineral elements in the trees and soils of the harvesting localities. To our knowledge, elemental analyses including Sr have not been directly reported on shellac resins.

Table 9. Multi-element analyses in trees hosted by *Kerria Lacca* insects compared to trees without insects. Mass concentration in ppm (Chen et al., 2005)

		N	P	K	Na	Ca	Mg	Cu	Zn	Fe	Mn
Flemingia macrophylla	Host branch	572.48	158.53	499.51	33.00	541.36	322.37	1.33	64.75	13.91	3.38
	Control branch	534.64	222.43	634.62	51.51	855.21	428.57	0.95	30.00	13.44	1.49
Albizia lucidior	Host branch	1088.65	643.81	337.86	43.17	1888.25	714.09	1.30	11.96	13.14	1.24
	Control branch	1182.67	489.70	412.90	54.06	1142.61	727.22	0.93	40.64	16.82	1.05
Schleichera oleosa 1	Host branch	324.07	236.76	545.27	25.63	2369.11	206.23	1.32	26.77	13.44	1.47
	Control branch	418.48	201.5	685.68	21.97	2390.77	246.38	1.70	20.15	13.86	1.90
Schleichera oleosa 2	Host branch	486.47	260.70	516.50	10.95	2674.11	341.12	1.68	26.50	11.13	1.67
	Control branch	453.39	179.00	797.10	47.37	1794.54	251.74	0.94	35.09	12.28	2.96
Koelreuteria paniculata	Host branch	732.02	261.80	333.90	36.58	825.66	194.88	0.95	12.16	14.40	1.48
	Control branch	1130.22	401.80	526.80	82.48	1044.61	248.09	0.93	45.79	13.64	1.87

4. Linseed oil/colophony varnishes

It was decided in this research to focus on linseed oil/colophony varnishes since 17th c. Italian violin varnishes, particularly Stradivarius, have been among the most widely studied musical instrument varnishes ever since the birth of a myth about their acoustic properties in the 19th c. (Bucur, 2016). This review considers the scientific knowledge on linseed oil before and after mixing with colophony, the drying processes, and then the aging of the varnish film (van der Doelen et al., 1998; Van den Berg, 2002; Wicks et al., 2007).

4.1. Linseed oil/colophony varnishes: organic binders

4.1.1. Molecular characterization of linseed oil

Vegetal oils are composed of linear triglycerides (TAGs), glycerol triesters, and fatty acids. TAGs comprise 3 branches of fatty acids linked to a glycerol molecule by ester bonds (Figure 20). Linseed oil contains saturated fatty acids: Stearic acids (S) (C18), Palmitic acids (P) (C16) and unsaturated fatty acids: Oleic acids (O), Linoleic acids (L), Linolenic acids (Ln)(Figure 21). The triglyceride LnLnLn is the most abundant. The composition depends on the geographical origin, climate, growing conditions, and refining (Wicks et al., 2007).

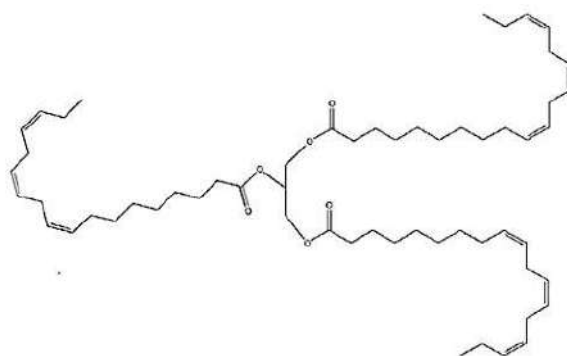


Figure 20. Molecule representation of a triglyceride LnLnLn

The polymerization of TAGs by reactivity with oxygen is carried out in the presence of 1,4-dienes (-CH=CHCH₂CH=CH-), i.e. diallylic methylene groups with 1,3-double conjugated bonds. However, saturated linoleic and linolenic acids have 1 or 2 diallylic methylene groups per molecule. Linseed oil is therefore one of the drying vegetable oils thanks to its high content of unsaturated fatty acids before drying and ageing (Wicks et al., 2007; Échard, 2010).

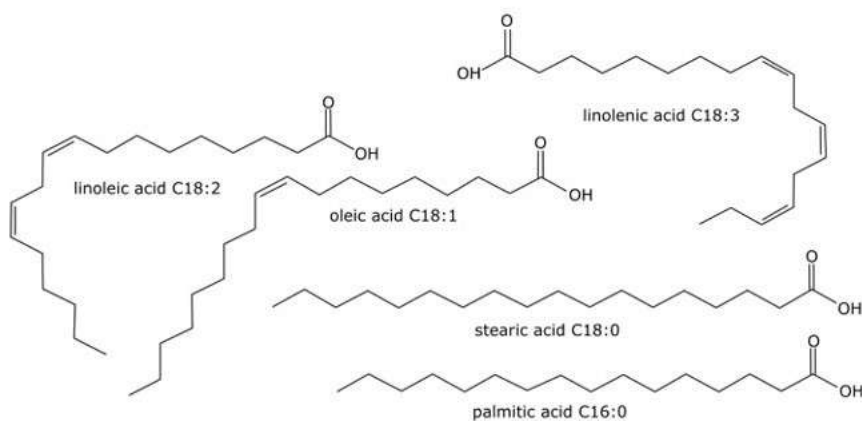


Figure 21. Molecules of saturated and unsaturated acids

4.1.2. Formation of the linseed oil/colophony varnish film

Recipes of linseed oil/colophony varnishes

Linseed oil/colophony varnishes are still produced today by some violin makers to reconstruct early varnishes based on written sources (Michetschläger, 2015, p.86). This approach can be completed by taking into account physico-chemical properties. The main parameters that can be adapted to obtain adequate rheological properties of varnish film are time, heating temperature and rosin proportions. Tirat et al. (2017) reported tests for the reconstruction of early linseed oil-colophony varnish with several temperatures and curing duration since the recipe ingredients are known, unlike the preparation procedure. The range of temperature tested was: 170°C – 250°C and the range of curing times tested was: 60 – 100 minutes. The most suitable parameters determined by these tests are presented in Table 10. Above a maximum proportion of 66.5%, colophony is no longer miscible in linseed oil (Tirat, 2015).

Table 10. Varnish preparations and rheological measurements on varnish films (adapted from Tirat et al., 2017)

Weight percentage colophony	Heating temperature (°C)	Heating time (min)	η_0 (Pa.s)	$\dot{\gamma}_c$ (s ⁻¹)	η_{1000} (Pa.s)	η_{35000} (Pa.s)	3t _c (s)
20	250	80	1.34	4666	1.31	0.18	n.d.
33	230	100	1.44	4180	1.40	0.17	89.4
20	250	100	3.07	2803	2.95	0.25	n.d.
50	230	100	6.85	1527	5.86	0.30	112.2
50	Violin-maker process ⁴³	n.d.	9.66	722	6.19	0.20	126.7
66	190	100	44.9	236	10.40	0.30	n.d.
58.5	230	100	54.2	308	16.6	0.48	529.8

During this PhD, linseed/oil colophony mixtures were prepared following the protocol developed by Tirat (2015). The pre-curing of linseed oil before the addition of powdered colophony is 1h for fresh linseed oil; however, this step was reduced to 30 min for a reference linseed oil dating from the bomb peak period in the 1960s. The mixtures were obtained using the following parameters: a heating temperature of 230°C, a heating time of 100 min, a proportion of colophony of 33% (Table 10). This proportion was chosen because the most widely studied early varnishes, which are from 17th c. Italian violins, were essentially made of a drying mixture of linseed oil (70%) and colophony (30%) (Weththimuni et al., 2016).

Varnish drying and polymerization of linseed oil

Roughly, the formation of the varnish film is due to the polymerization of TAGs that occurs in 3 steps (Wicks et al., 2007)(Figure 22):

- 1- Initialization stage:
Decomposition of hydroperoxides into free radicals which will first consume antioxidants
- 2- Auto-oxidation stage:
Increasing content of hydroperoxides and appearance of conjugated dienes after reaction of 1,4-dienes (-CH=CHCH₂CH=CH-) with free radicals and then with oxygen.
- 3- Cross-linking reactions:
Decomposition of hydroperoxides into free radicals, resulting in a chain cross-linking reaction

⁴³ Varnish recipe communicated by Tony Echavidre, violin-maker (Bordeaux, France), Tirat, 2015

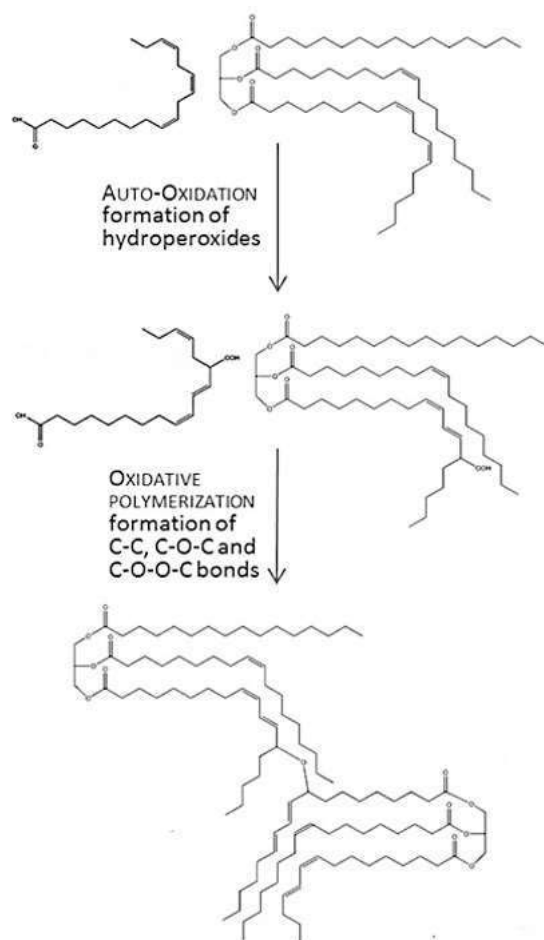


Figure 22. Description of the drying process (adapted from Tirat, 2015)

Interaction linseed oil – colophony

Tirat (2015) reported the siccativ properties of colophony in oil-colophony varnishes with suitable proportions for the formation of varnish film. The polymerization process of linseed oil which involves colophony is not yet sufficiently understood to explain the properties of linseed oil/colophony varnishes compared to those of drying linseed oil alone. Current knowledge on the interaction between colophony and linseed oil during the preparation and drying stage of the varnish is presented in [Appendix 1](#).

4.1.3. Alteration of the linseed oil/colophony varnish film

The oxidation processes of each compound are discussed here. Further research should be carried out in the near future on the complex interactions between the oxidation products of colophony and linseed oil (Tirat, 2015).

Oxidation of colophony

Oxidation reaction mechanisms are discussed in the literature to assess the complex state of oxidation of resins in oil-based varnishes (Berg et al., 2000; Scalarone et al., 2002; Courel, 2016; Dietemann et al., 2009)(Figure 23). The main product, dehydroabietic acid (DHA), produces oxidized forms such as 7-oxo-DHA (Tirat, 2015).

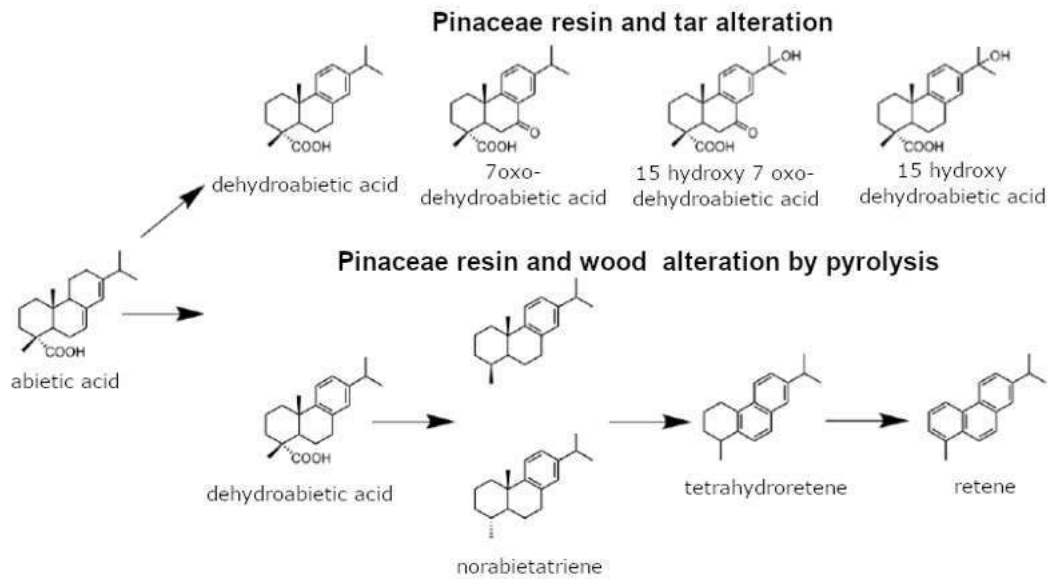


Figure 23. Abietic acid alteration mechanism (adapted from Courel, 2016)

Oxidation of linseed oil

Two mechanisms for the oxidation of linseed oil are described in the literature (Malléjol et al., 2000; van den Berg, 2002)(Figure 25):

- Chain breaking (hydrolysis / free radical mechanisms)
- Oxidation of unsaturated fatty acids

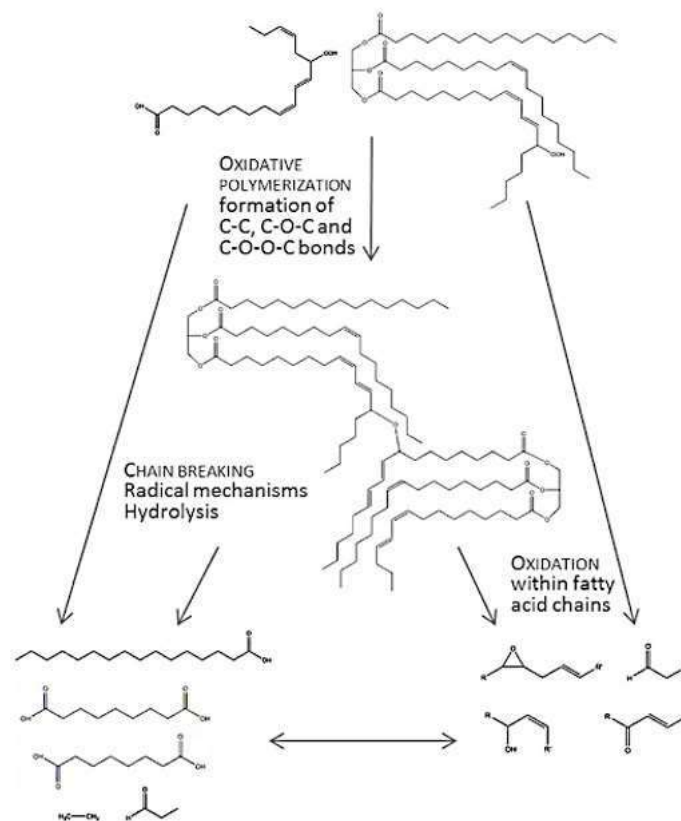


Figure 24. Oxidation processes of triglycerides in oil-based varnishes (adapted from Tirat, 2015)

Oxidation of linseed oil-colophony varnishes

The molecular composition of varnishes after natural oxidation depends on different parameters including the ingredient ratios or environmental conditions (such as photo-oxidation). The impact of long-term natural ageing is still difficult to apprehend and remains controversial in modelling using artificial ageing processes (Dietemann et al., 2009). Mixtures of linseed oil and colophony yield groups of polymers with a complex global structure due to successive processes of polymerization, co-polymerization, chain breaking, as well as the mixing with oxidation products such as free diterpenes or other compounds with undefined polymeric interactions (Azémard, 2014; Decq et al., 2021).

Moreover, the rate of oxidation varies according to the distance from the external surface inducing material heterogeneity with more or less altered parts marked by chemical differences. However, biomarkers that are stable over time can be used for material characterization, dating and provenance studies despite complex oxidation processes (Courel et al., 2017).

- Triglycerides with linolenic acids (LnLnLn) are the most abundant in linseed oil.
- The formation of the linseed oil/colophony varnish film is possible thanks to the polymerization of TAGs. Colophony has a siccative effect in interaction with TAGs.
- The oxidation of linseed oil/colophony varnishes is complex (also involving interactions between oxidation products and volatile fragments) and controversially modeled using artificial ageing.

4.2. Linseed oil/colophony varnishes: driers and pigments

Linseed oil/colophony varnishes may also be more or less contaminated by adding driers as well as organic and/or inorganic pigments.

4.2.1. Driers

The drying of an oil-based varnish is catalysed by metallic salts (also called driers) such as manganese, zirconium, rare earths, cobalt, and lead and mixed with the varnish before application (Wicks et al., 2007). Von Bohlen (1999) attributes the presence of Pb, Mn, Co to the addition of some driers to accelerate the natural drying process of siccative vegetal oils. UV light from sunlight was also commonly used for the same purpose, otherwise violin makers would have had to wait for several months in order to obtain a hardened varnish.

Litharge (lead white or lead monoxide, PbO) was one of the most widespread driers in modern Europe. However, based on 37 analyses performed on historical varnishes, Echard (2010) notes that it is not possible to conclude on a systematic use of lead-based driers in oil varnishes (Figure 25).

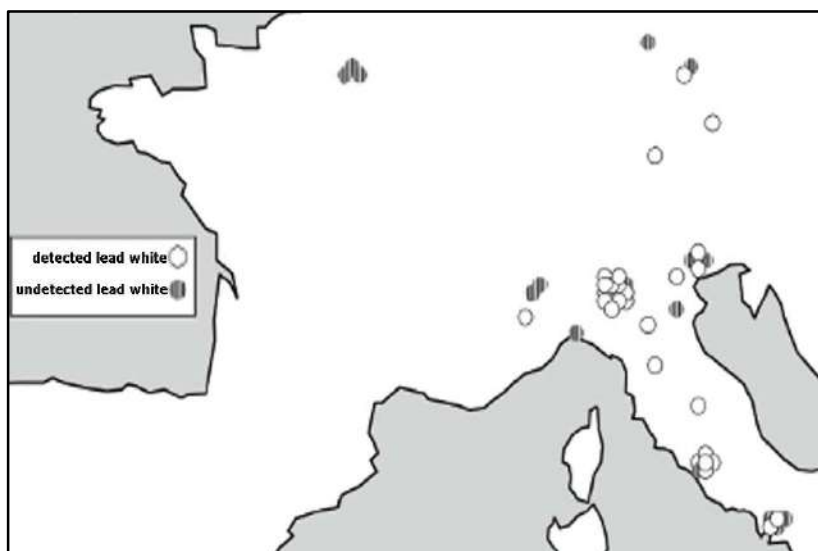


Figure 25. Distribution of varnishes with and without lead in Europe (Echard, 2010)

4.2.2. Pigments

4.2.2.1. Pigments in violin making

Metallic compounds and other trace inorganic elements may have been introduced into oil-based varnishes by driers, organic binders, but also by the addition of pigments, either as an underlying layer to the varnish or mixed with the varnish before application (Figure 26).



Figure 26. Optical image of the varnish of the "Sarasate", violin, Stradivari, Cremona, 1724, Musée de la Musique, E.1729, with scattered vermilion grains (Echard, 2010)

Von Bohlen et al. (2007) reported a series of elementary composition analyses on early violin varnishes. Analyses using total reflection X-ray fluorescence spectroscopy for ultra-trace element analysis (TXRF) revealed, for instance, the concentration of S, Cl, Ar, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Pb, Br, Sr in the original varnish of a Guarneri violin c. 1670, Cremona (von Bohlen and Meyer, 1997). In another study, von Bohlen (2004) compared the trace element concentration in three alcohol and oil based varnishes (Table 11). Analysis using μ PIXE (Particle-Induced X-ray Emission) revealed the varnish content in Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Ag, Cd, Sn, Ba, and Pb (von Bohlen et al., 2007). These chemical elements come from the addition of different materials such as pigments, metal salts, and organic binders to the varnish, but the specific contribution of each compound has not been studied. Using Principal Component Analysis (PCA), von Bohlen (1999) suggested using trace

element ratios to highlight signatures that could be attributed to some well-known makers or early manufacturing centers.

Table 11. Quantitative results of TXRF analysis of 3 historical varnishes (adapted from von Bohlen, 2004). Mass given in ppm. n.d. not determined (below detection limit)

Element	Drying oil from a piece of German furniture c.1800	Spirit 1 from a wooden Banister in German house 1902	Spirit 2 from a Bohemian double bass c.1900
K	4,480	180	670
Ca	13,700	1,860	6,880
Ti	250	n.d.	n.d.
Cr	30	n.d.	n.d.
Mn	740	186	29
Fe	3360	575	450
Ni	26	10	21
Cu	51	22	39
Zn	630	285	150
As	n.d.	n.d.	490
Rb	13	n.d.	n.d.
Sr	57	n.d.	150
Ba	560	180	4,360
Pb	1,480	3,250	2,810

4.2.2.2. Pigments in horse-drawn carriages

The concern of carriage painters was to reduce drying times, to use affordable and compatible materials while maintaining the mechanical and weather-resistant quality of the painted surfaces. Pigments and organic binders are ideally cheap and siccative; lead white was often added for these properties and also to reduce the yellowing of the diterpene resin. Here are some pigments detected on sleds studied during this PhD. More details on commonly used pigments can be found in the literature (Devergne, 1993).

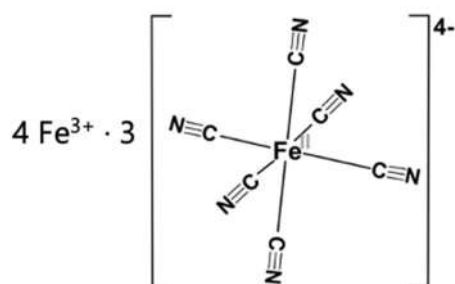
Carmine lacquer

Carmine lacquer (or Florentine lake) and madder lacquers are obtained by mordanting a natural red dye such as kermes, cochineal or madder. Cochineal is too expensive, so kermes was more often used. The precipitation of kermes in boiling water to extract carminic acid ($C_{22}H_{20}O_{13}$) is completed with alum ($KAl(SO_4)_2 \cdot 12H_2O$), iron sulfate (“Vitrioli Martialis”), and potash (“sale alcalico Tartari”). This pigment is expected to comprise carbons that are contemporaneous with the fabrication process without an aging impact on the ^{14}C dating.

Prussian blue

Prussian blue (or ferric (III) hexacyanoferrate(II)) has the following formula: $Fe(III)_4[Fe(II)(CN)_6]_3$. It was discovered accidentally during the synthesis of Florentine lake c.1704 in Berlin and was widely traded in Europe during the 18th c. (Kraft, 2008). The color maker Diesbach used potash (potassium carbonates) reconditioned by M. Dippel contaminated with hexacyanoferrate after distillation of animal blood. According to early recipes, crude tartar (potassium hydrogen tartrate) was added to crude nitre (potassium nitrate) and charcoal. Then, extemporaneous alkali or potash was added to ox blood. After a calcination step, vitriol (iron sulfate) was added with crude alum ($KAl(SO_4)_2 \cdot 12H_2O$) (Kraft, 2009) (Samain et al., 2013). The making processes

have changed over time⁴⁴. The triple bonds between carbon and nitrogen are resistant to acid leaching in the usual protocol of ¹⁴C decontamination prior to radiocarbon dating (i.e. “A” treatment, see methodological part, Chapter 3 – § 4.1).



Lead white

Lead white is a synthetic pigment containing lead carbonates involving CO₂ (organic carbon from animal waste), lead and vinegar, and a mineral pigment with cerussite PbCO₃ and hydrocerussite 2Pb(CO₃).Pb(OH)₂. Geological carbons have to be separated by thermolysis from organic carbons which is contemporaneous with the period of manufacturing of the lead white pigment (Messenger, 2020). Naples yellow contains lead white.

Chalk

Chalk (CaCO₃) is a natural mineral deposit comprising calcium carbonates. Gypsum (CaSO₄·2H₂O) is a hydrated calcium sulfate that could also be used as a filler and a white pigment. However, it does not induce a ¹⁴C contamination with geological carbons such as carbonates in chalk.

Verdigris

Verdigris is a synthetic pigment containing copper carbonate Cu₂CO₃(OH)₂ involving acetic acid and copper, or formed by the weathering of copper. It can be made of copper acetates Cu(CH₃CO₂)₂. The oxidizing agent in the manufacturing process can be vinegar, acetic acid, wine, atmospheric air and induces the incorporation of contemporaneous carbons.

- Lead white is often used as a drier and a pigment.
- ¹⁴C dating can be contaminated by driers and pigments. However, the impact is difficult to determine.

⁴⁴ Analyse par spectroscopie Mössbauer et par spectroscopie d'absorption X du bleu de Prusse, L. Samain, M. T. Sougrati, F. Grandjean, G. J. Long, F. Hatert, D. Strivay en collaboration avec G. Silversmit (XMI group, Université de Gand), Rapport annuel CEA, (2009).

5. Conclusion

Natural resins used in varnishes are all of plant origin (except for shellac, a derivative from *Kerria lacca* insects fed on trees). Resins were adapted for the making of varnishes depending on the geographical distribution of species in the world, the historical period and the trade developments. For example, turpentine and colophony were mainly extracted from Pinaceae species (as well as some species from the Larix, Abies and Picea families) in Europe, and widely used in early varnishes for violin making and carriages until at least the 18th c. The chemical differentiation between natural resins is related to the botanical origin of the plant; biomarkers can be used as indicators to distinguish them from one another (Figure 27, Table 12). For example, the main molecules in colophony are abietic and pimaric acids, especially dehydroabietic acid (DHA) after natural oxidation (Mills and White 1987). When applying ¹⁴C dating to natural resins, the measurements may be an accurate indication of the varnish-making period due to the short storage duration (Chapter 1– § 3.4). However, subfossil and fossil resins such as subfossil copals and amber can induce high contamination. Regarding isotopic geochemistry applied to natural resins, elemental compositions have been investigated in the literature according to the content in % (major), ppm (minor) and ppb (traces). Sr is often detected at ppm level with slight variations between the tree organs (leaves, trunk, roots, ...).

Natural early oil-based varnishes are mixtures of triglycerides of linseed oil and molecules of natural resins that have siccative effects. After curing, application and polymerization of the varnish film, ageing processes lead to a complex mixture of polymers and oxidation products. During oxidation, exchanges with the atmosphere are not expected to impact the carbon content and the application of ¹⁴C dating on varnishes. A feasibility study of ¹⁴C dating at the molecular scale on linseed oil-colophony varnishes was conducted to date ingredients separately. The LSCE has a GC-Prep to separate and collect sufficient quantities of biomarkers before dating. Unfortunately, organic chemistry analyses on colophony and linseed oil showed that a separation would require derivatization i.e. adding exogenous ¹⁴C. This step is not compatible with the precision required to yield conclusive results. Moreover, further bibliographical research following the tests highlighted the interactions between colophony and linseed oil. The formation of an adduct in the linseed oil/colophony mixture between the two ingredients limits the possibilities of retrieving the initial molecules (Appendix 1).

In the following, during this PhD study, ¹⁴C dating was applied on “bulk” early varnishes. Possible contaminations of ¹⁴C measurements by driers and pigments have to be taken into account. The study of their impact is part of ongoing research that involves ¹⁴C dating and material characterization analyses. For example, lead white used as a drier and a pigment is associated with recent ¹⁴C dating research in the field of Heritage science (Hendriks et al., 2020; Messenger, 2020).

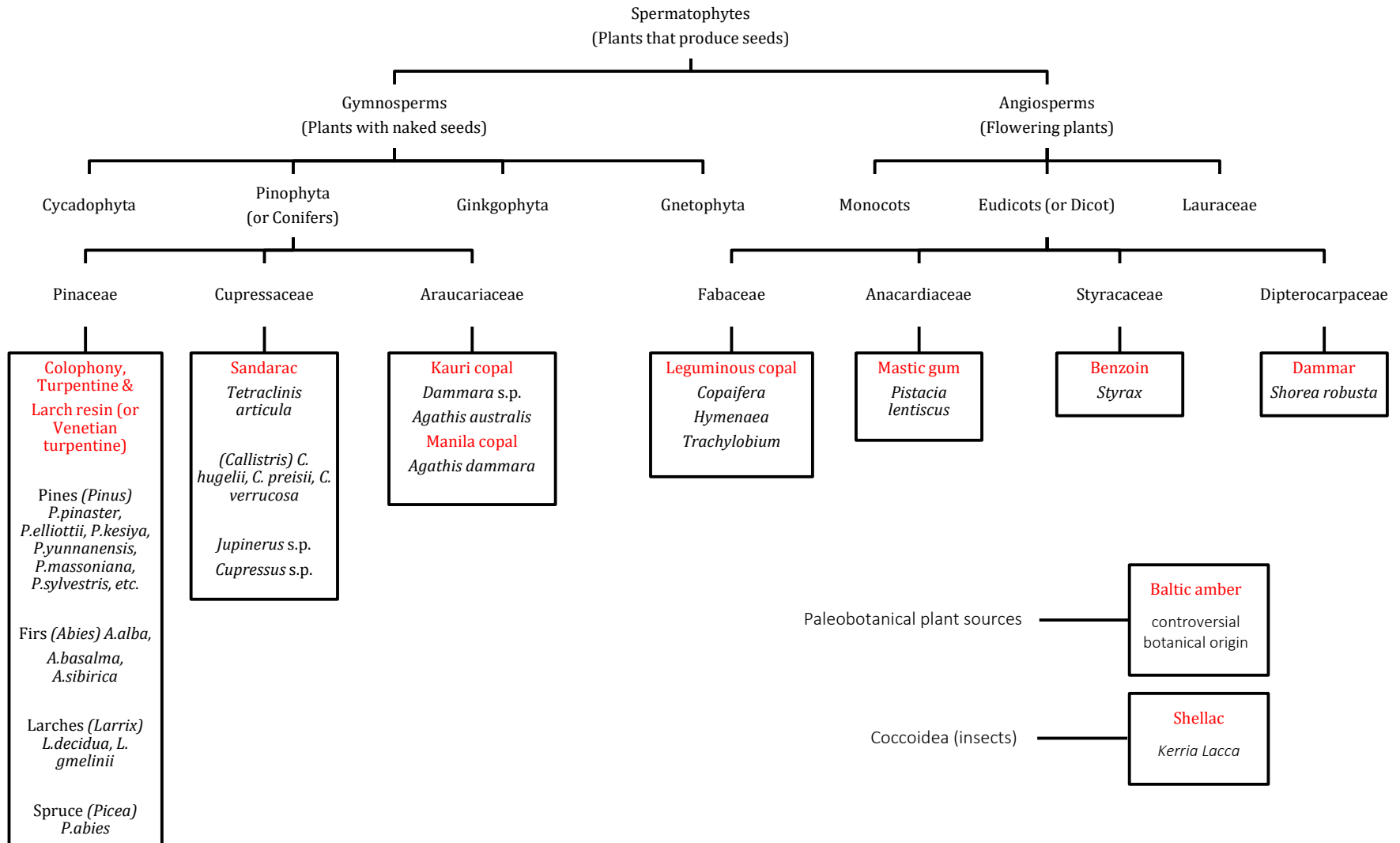


Figure 27. Extract from the classification of the botanical families producing natural resins used in violin making according to their groups in the plant kingdom, gymnosperms including conifers and angiosperms (or flowering plants) (Regert et al., 2008; Decq, 2021)

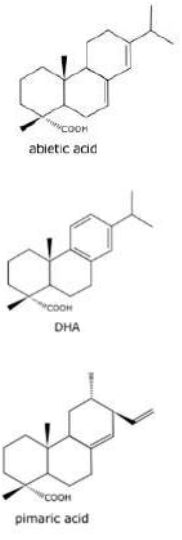
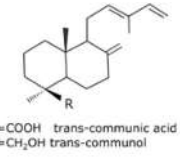
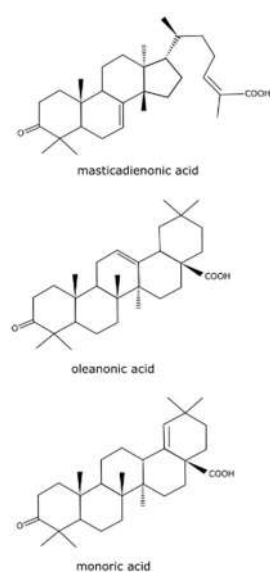
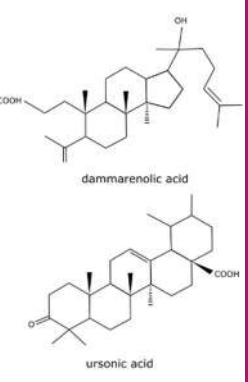
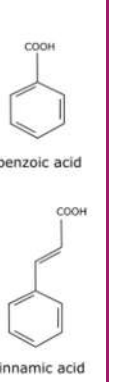
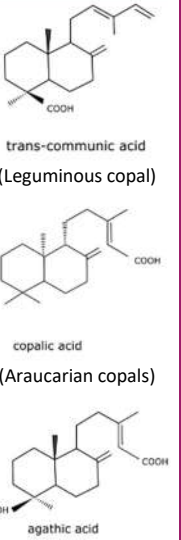
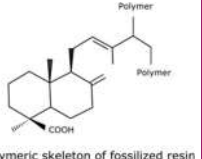
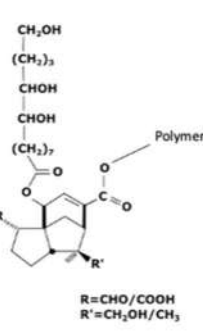
	Colophony	Sandarac	Mastic gum	Dammar gum	Benzoin	Copal	Baltic amber	Shellac
Class	Diterpenoid resin	Diterpenoid resin	Triterpenoid resin	Triterpenoid resin	Phenolic resin	Diterpenoid resin	Diterpenoid resin	Aliphatic resin with sesquiterpenes
Main organic composition	(Abietanes) abietic, neoabietic, palustric acids, dehydroabietic acid (DHA) (Pimaranes) pimaric acid, isopimaric acid, sandaracopimaric acid	(Labdanes) polycommunic acid polymer	(tetracyclic) masticdienonic acid (pentacyclic) oleanonic, moronic acids	(tetracyclic) dammarenolic acid (pentacyclic) ursonic acid	benzoic, cinnamic acid coniferyl benzoate	(Leguminous copal) ozic, eperuic, copalic, guamaic, oliveric and daniellic acids (Araucarian copals) sandaracopimaric, agathic acids	(highly polymerised structure of labdanes) communic, succinic acids	aliphatic acids linked to cyclic terpenes
Main molecules	 <p>abietic acid</p> <p>DHA</p> <p>pimaric acid</p>	 <p>R=COOH trans-communic acid R=CH₂OH trans-communol</p>	 <p>masticdienonic acid</p> <p>oleanonic acid</p> <p>moronic acid</p>	 <p>dammarenolic acid</p> <p>ursonic acid</p>	 <p>benzoic acid</p> <p>cinnamic acid</p>	 <p>trans-communic acid (Leguminous copal)</p> <p>copalic acid (Araucarian copals)</p> <p>agathic acid</p>	 <p>polymeric skeleton of fossilized resin</p>	 <p>R=CHO/COOH R'=CH₂OH/CH₃</p>

Table 12. Recapitulative table for the molecular composition of natural resins in violin making.

CHAPTER 3. Contribution of ^{14}C geochronology to knowledge of the uses of Heritage objects including coatings and strings

1. Introduction

One objective of this PhD research was to evaluate the feasibility of applying ^{14}C geochronology to date the period of manufacture and different interventions on musical instruments and other Heritage objects. To do so, we decided to focus especially on the dating of the varnish stratigraphy as well as on lacquered pieces of furniture and horse-drawn carriages.

This chapter presents the results obtained using ^{14}C dating on mechanically separated layers of “bulk” varnishes, i.e. comprising inorganic and organic compounds. As we had previously invalidated the ^{14}C dating approach at the molecular scale, we initially tested the “bulk” approach on lab-prepared mixtures and then on historical linseed oil/colophony varnishes. Physical measurements of residual ^{14}C activity were done on the compact radiocarbon system (ECHO MICADASTM by Ionplus) operated at LSCE by the GeoTrAc group. Material analyses were done on equipment present at CRCC, LRMH and the Musée de la musique (CRC UAR3224). Some of the ^{14}C dating measurements were also conducted on gut strings of stringed instruments as material evidence of the periods of (musical) use of the objects. I was personally involved during each step of the micro-sampling interventions and almost all analyses in material characterization, as well as during chemical pre-treatments.

The chapter is divided into the following parts: the general methods with their expected limits and the protocols with tips and adaptations (part 1); the historical, material and ^{14}C dating analyses obtained for each selected Heritage object in private or museum collections (part 2); and finally the discussion and interpretation of the results (part 3).

2. Methods – general principles

During this PhD, the multidisciplinary framework combined ^{14}C geochronology with museum expertise. The general methods discussed here are conventional scientific approaches used in museum institutions, including historical documentation and material characterization analyses (§ 2.1), and radiocarbon dating (§ 2.2).

2.1. Conventional museum expertise

Stringed instrument making is imbued with a long oral tradition. Thus, the instruments are seldom associated with detailed direct written sources and their materiality is an important source of documentation (Chapter 1 – § 2.3). Owing to their complex materiality (Chapter 1 –

§ 2), musical instruments and other Heritage objects need to be documented by combining museum expertise, which includes restoration, conservation, organology, history, and instrument making, with classical or advanced analyses in material sciences. A similar strategy is applied specifically on early varnishes due to their complex composition and distribution both in surface area and in thickness after natural ageing and anthropic actions including wear, restoration, retouching, re-varnishing, maintenance or counterfeiting operations, etc. Echard (2010, p.85) reviewed the most common analytical principles for examining musical instrument varnishes.

The preliminary steps in the development of a methodology for analyses on a Heritage object kept in the collections of French museums begins with the consultation of its “dossier d’oeuvre”. This consists of documentation collected in museums about current scientific knowledge on an object and its material history. The main objectives are for example to better understand the materials, early making practices, alterations and the chronology of restoration treatments in order to develop reconstructions or conservation strategies. The collected data may provide information on the identity of the inventoried object, the date of entry in the collection, the mode of acquisition such as public auction or donation, etc. In fact, the list of documents is not exhaustive, and also includes archives, exhibition catalogues, related publications on the object or on a comparative corpus, state of conservation reports, invoices of restoration interventions, reports of informal emails/discussions between curators, experts or previous owners, etc. Published or unpublished reports of analyses can also be found using methods such as dendrochronology, botanical identifications, stylistic comparisons, written sources, X-ray digital radiography, endoscopic analysis, etc. (Durier et al., 2019a). As an example, a database with dendrochronological results on bowed instruments kept at the Musée de la musique was consulted during this PhD. The term of “dossier d’oeuvre” is used in the museum context. However, information is also collected for objects from private collections according to the practices of other professionals (instrument makers, auctioneers, etc.). The accessible documentation gathered about a private or museum object can be scarce for several reasons, but it is a knowledge base for researchers who focus on acquiring new data in accordance with their research aims using a wide range of museum approaches and scientific tools.

Analyses routinely performed on Heritage materials are preferentially “non-invasive” i.e. *in-situ* non-destructive approaches (not requiring sampling), then come non-destructive analyses on micro-samples and lastly micro-destructive analyses (Figure 28). The most suitable analytical techniques are chosen according to an initial specific question, time and financial resources, partnerships or the accessibility of scientific equipment. Micro-sampling is only decided if warranted by the importance of the information to be acquired and a minimum sample size needs to be reached using the selected technique (close to the detection threshold). We note here that all scientific tools have inherent analytical limits in their applications and are complementary to deepen the scientific knowledge on materials. Strategies continue to be developed in material sciences to study the complex stratigraphy and distribution of the varnishes, as reported by Invernizzi et al. (2019), and other techniques are tested using exploratory approaches.

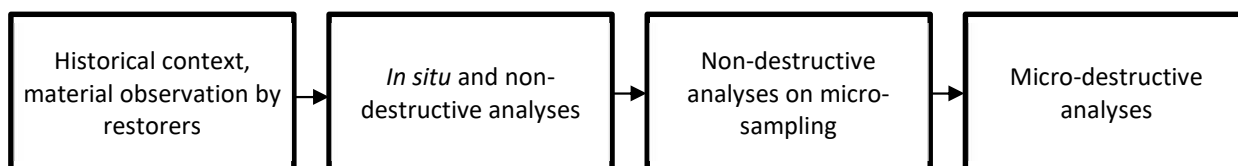


Figure 28. Methodology currently followed by order of priority for material analyses on Cultural Heritage objects.

The different material characterization techniques used during this PhD study are discussed below (Durier et al., 2021). The description of the equipment is presented in [Appendix 2](#).

- Visual examination and *in situ* VIS/IR/UV imaging (Figure 29): an upstream visual examination of historical varnished objects comes first, mostly performed by restorers or musical instrument makers, in order to identify a representative area to study. The varnish surface is observed under several lights, essentially under UV light, to better apprehend the stratigraphy and identify original materials due to different luminescence properties. At this step, high-resolution photography can be used as well as magnifying glasses or a binocular microscope.
- Optical microscopy on micro-samples for stratigraphic observations.
- Energy dispersive X-ray fluorescence spectrometry (XRF) for *in situ* analyses or on micro-samples is dedicated to the analyses of inorganic compounds in varnishes such as pigments, driers, inks, etc.
- Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM–EDS) combines microscopy and X-ray fluorescence spectrometry at a microscale to study the stratigraphy and the inorganic composition of varnishes.
- Fourier Transform InfraRed spectroscopy (FTIR) is used for non-destructive analyses of organic materials on micro-samples.
- Raman spectrometry is applied for analyses of both organic and inorganic materials on micro-samples.
- Gas chromatography–mass spectrometry (GC-MS) is micro-destructive and semi-quantitative and is applied for the identification of organic molecules in varnishes.

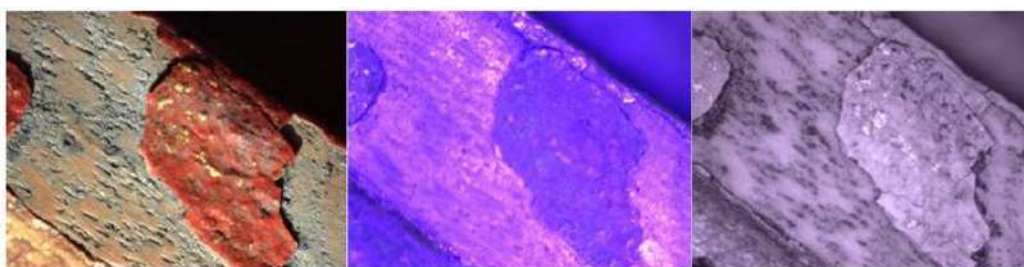


Figure 29. (from left to right) Pictures under visible, UV and IR light of a varnish surface on the red and gold sled, inv. TR1868, coll. KMKG-MRAH (§ 6.4.6).

2.2. Radiocarbon dating

The principles of the ^{14}C dating method have been widely published, both in specialized scientific journals (Libby et al., 1949; Libby, 1967; Cain and Suess, 1976; Bonani, 2000; Hajdas, 2008; Hajdas et al., 2021) and in journals for the general public (e.g. Fontugne, 1996). Here, I will only discuss the points of interest for our study. The principle of ^{14}C dating is based on

measurement of the activity of the radioisotope of carbon, carbon-14, naturally present in organic and inorganic matter in trace amounts, in relation to the most abundant stable isotope of carbon, carbon-12 (^{12}C). The ^{14}C isotope, formed in the upper atmosphere as a result of cosmic radiation $^{14}\text{N} + ^1_0\text{n} \rightarrow ^{14}\text{C} + ^1_1\text{H}$, is found throughout the carbon cycle (atmosphere, oceans, biosphere). It is absorbed by living organisms, then follows a radioactive decay as soon as the individuals die with a decay period about 5730 years, which makes this radioactive element a good chronometer for the last 50,000 years.

The classical equation (1) that links the time elapsed since the death⁴⁵ of the sample, so called "age", and the residual ^{14}C activity should then apply:

$$\mathbf{age} = -T * \ln(A/A_0)/\ln(2) \quad \mathbf{eq. 1}$$

with T the ^{14}C decay period, A_0 the original ^{14}C activity, and A the measured residual ^{14}C activity. However, because the atmospheric ^{14}C content that should correspond to A_0 has varied greatly over the last 50,000 years (e.g. Reimer et al., 2020) and because the decay period, T, is not that well known (Kutschera, 2019), the calculation of "age" is not direct but must first go through an empirically obtained abacus, called " ^{14}C calibration". The historical evolution of the calibration curve was recently drawn by Reimer (2021) and the latest calibration curve, IntCal20, is presented in Reimer et al. (2020).

The residual ^{14}C activity is expressed with different units. The recommended one (Reimer et al. 2004) is $F^{14}\text{C}$ which reports the raw measurement as a ratio to an international standard and normalized to $\delta^{13}\text{C}$ of -25‰ to account for isotopic fractionation between organisms that results in a ^{14}C content that differs from one organism to another:

$$\mathbf{F^{14}C} = (A_S \cdot A_{OX}/0.95) \cdot (0.975/0.981)^2 \cdot [(1 + \delta^{13}\text{C}_{OX}) / (1 + \delta^{13}\text{C}_S)]^2 \quad \mathbf{eq. 2}$$

where A is the activity or $^{14}\text{C}/^{12}\text{C}$ isotope ratio, and subscripts S and OX refer to sample and oxalic acid standard, respectively. $F^{14}\text{C}$ is unitless. In memory of the 1950s, and the time when Willard Libby was awarded the Nobel Prize for his discovery of the ^{14}C dating method, residual ^{14}C activity is also expressed as " ^{14}C conv. age". The unit is "conventional radiocarbon years before AD 1950", or briefly "year before present" and abbreviated to "BP" (Radiocarbon journal, instructions for author, section 7.2).

$$\mathbf{age} = -5568 * \ln(F^{14}\text{C})/\ln(2) \quad \mathbf{eq. 3}$$

This way of expressing ^{14}C activity is ambiguous. It suggests that the result of equation 3 is a real age. But a " ^{14}C conv. age" is not a duration of time elapsed since the death of the organism. The duration of a ^{14}C year even fluctuates, going from 1/3 to three times the duration of a real year (Bard et al., 2020).

Conversely the transcription of the measured residual ^{14}C activity into calendar age, using the ^{14}C calibration curve, yields a real duration and the calendar age is a real age. The unit is "cal BP" for "calendar year before present".

⁴⁵ death = instant from which the direct (photosynthesis) or indirect (feeding) interactions between the sample and the atmosphere are broken.

2.3. Overcome and expected obstacles

On the one hand, musical instruments comprise a range of organic materials from diverse periods, such as gut or silk wires, varnishes or some species of wood, that are impossible to date with the scientific techniques commonly used in Cultural Heritage institutions (such as dendrochronology, comparison with iconographical sources, etc.). For example, dendrochronology cannot be carried out on too short tree-ring record or some wood species ([Chapter 1 – § 4.3](#)). On the other hand, radiocarbon dating is widely used in the fields of archaeology and paleoclimatology; however, it is underused for studies that postdate AD 1500. The number of ^{14}C studies on musical instruments made during the modern period, i.e. from the 16th c. to the 19th c., is limited (Chase et al., 2009; Durier et al., 2019a, 2021). Indeed, there are three obstacles to tackle.

Obstacle 1: sampling size

Based on the restrictions in the field of conservation of Cultural Heritage objects and the detection limit of the compact radiocarbon dating system, ECHoMICADAS, the sample size may not exceed a few hundred micrograms. Non-invasive and non-destructive analyses are usually preferred by curators, but micro-sampling is tolerated as long as the aesthetic integrity of the object is respected ([§ 2.1](#)).

50-100 μg of carbon is required for ^{14}C measurements with sufficiently high precision to obtain ^{14}C dating that can distinguish historical times ([see obstacle 3](#)). Linseed oil/colophony varnishes contain around 70%wt C, thus, a micro-sampling of $\sim 100 \mu\text{g}$ of varnish is theoretically sufficient, i.e. 5 mm^2 for a film thickness of 20 μm . Under real conditions, including the risk of material loss during the purification of the sample, a sampling of 1 mg is targeted, i.e. 0.5 cm^2 for a film thickness of 20 μm . Measurements on these small samples are made via the MICADAS gas source. If enough material is available, we will make as many measurements as possible, in order to reduce the measurement uncertainty by statistics. When there is less limit of mass in the sampling, we will rather aim at the solid source (mass > 500 μg of carbon) to improve the precision of the measurement.

Obstacle 2: complex chemical environment

The initial composite constitution of musical instruments (varnishes, glues, strings, wood pieces, etc.) is even more complex as they have undergone modifications over time ([Chapter 1 – § 2](#)). The interpretation of the ^{14}C measurements on varnish stratigraphy is possible when:

- * micro-samples have been properly taken and localized with the assistance of an expert (restorers, instrument makers, etc.)
- * successive varnish layers have been documented thanks to material characterization approaches
- * micro-samples have undergone specific and complex chemical protocols to select the carbon to be dated. The purity of the CO_2 gas produced depends on the quality of the upstream chemistry, otherwise perturbations will occur at the ECHoMICADAS ionisation. The chemical protocol should also help in distinguishing (and separating) carbon from different sources (and thus different ages).
- * historical documentation completes the knowledge on the materials and craft practices from the past (such as the average duration of organic binder storage), as well as the origin of the

historical object on which the varnish was sampled, thanks to history of technology and archive studies.

Obstacle 3: complex calibration curves

Due to the high fluctuation of initial atmospheric ^{14}C content caused by various parameters (solar activity, earth magnetic field, etc.), the historical period may be considered as unfavourable to radiocarbon dating. The calibration curve is complex, leading the measured residual ^{14}C activity to be converted into several equiprobable ranges of calendar dates (Reimer et al., 2020)(Figure 30). For calibration in the period studied here, the 19th c. is the most difficult to apprehend using ^{14}C dating and the only solution left will be to accumulate samples measured with ^{14}C dating compared with other constraints of time gaps such as tree ring counts, knowing that the "spike" around 1800 could possibly be reached in some study cases.

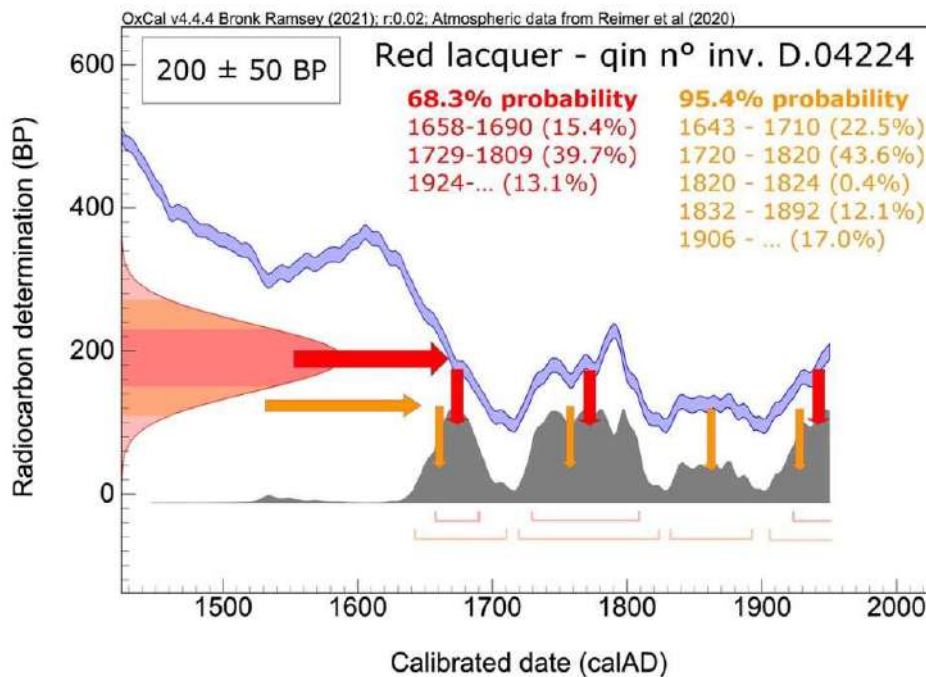


Figure 30: Example of calibration using the IntCal20 curve on a red lacquer from a qin n° inv. D.04224 from the CNAM collections with a $F^{14}\text{C}$ of 0.976 ± 0.007 (modified from Durier et al., 2021)

The smaller the sample size, the lower the precision of the equiprobable intervals; the larger the sample, the higher the counting statistics in the MICADAS and the smaller the measurement uncertainty (Figure 31). In the present research, the $F^{14}\text{C}$ uncertainty can be as low as ± 0.002 for the largest samples (1mg of carbon). Among the smallest samples analyzed (0-40 μg C), the $F^{14}\text{C}$ uncertainty was ± 0.007 .

The most favourable dating ranges for radiocarbon dating are [1600 - 1730] or [1770 - 1810].

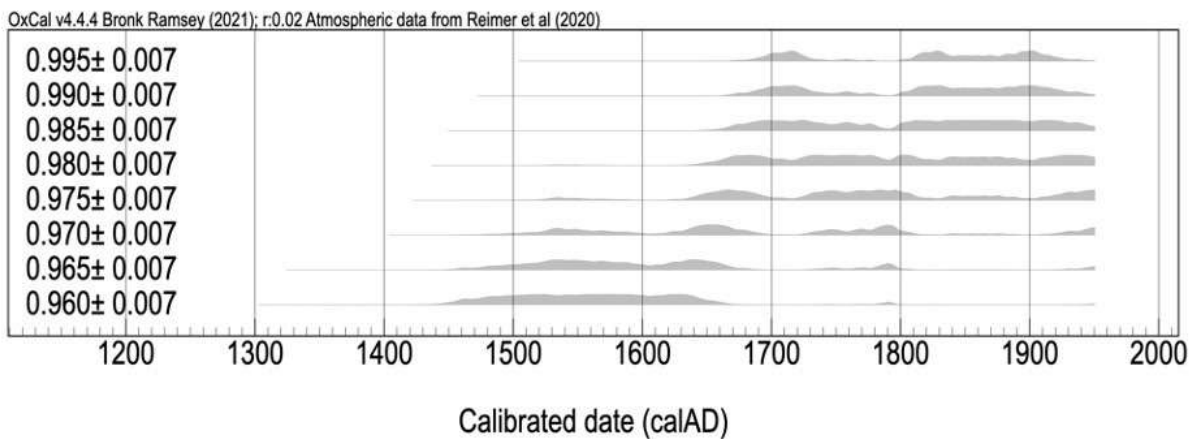
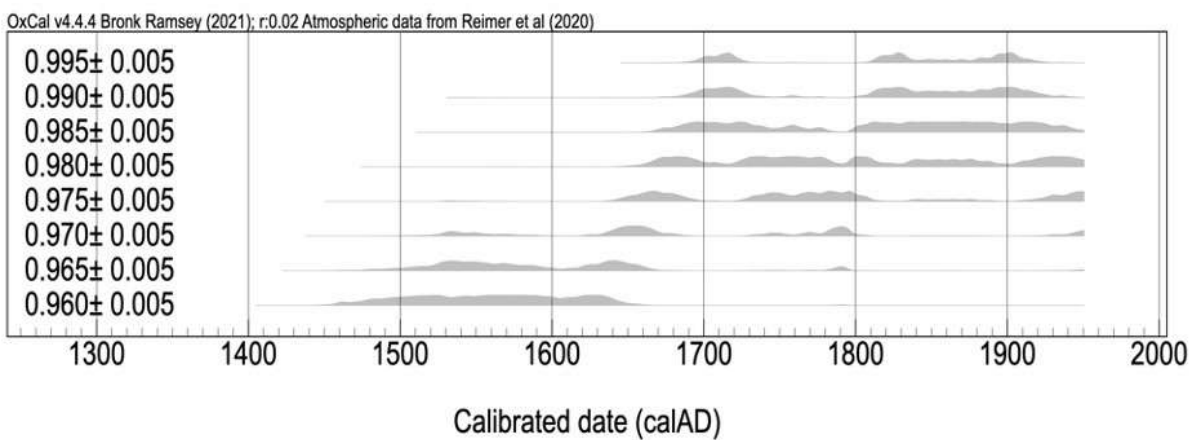
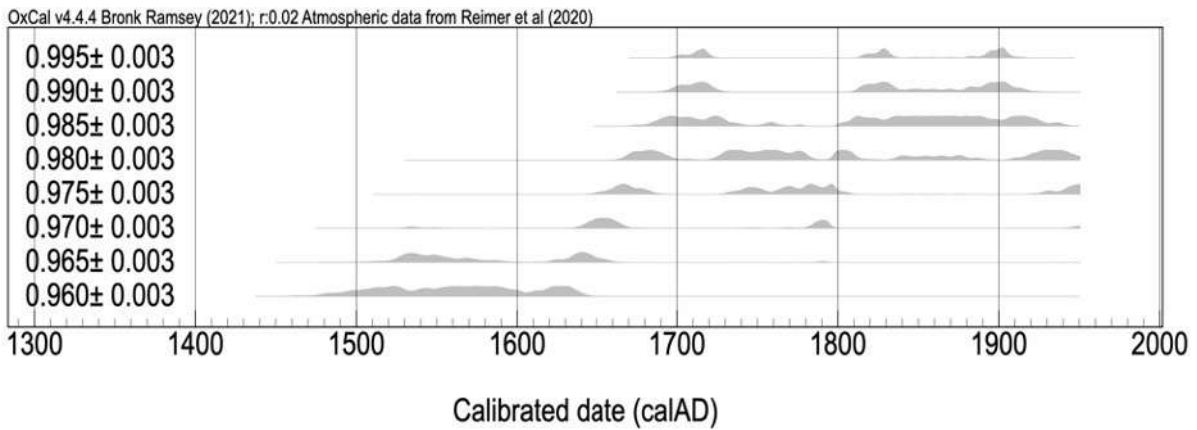


Figure 31: Impact of the size of the sample on the ^{14}C age measurement for several examples of residual radioactive activity measurements using IntCal20.

3. Sampling protocols

As presented in the historical state of the art on early varnishes, musical instruments and other Heritage objects such as horse-drawn carriages were commonly covered with several layers of varnish through successive periods. One of the aims of this study was to separate the layers to

be dated using radiocarbon dating, such as the separation of an upper maintenance layer from the original varnish layer.

The sampling methodology was complex to define and to apply as violin makers and restorers have extensive expertise using solvents to separate successive layers, e.g. to separate an upper layer of alcohol-based varnish and a lower original layer of oil-based varnish. However, organic solvents should be proscribed when performing ^{14}C measurements due to possible carbon contamination by dead carbon if the solvent derives from petroleum or by actual carbon if the solvent is bio-based. Thus, different mechanical sampling methods were tested using chisels.

3.1. A preliminary case study

Firstly, varnish sampling on a violin, Pierre Saint-Paul, c.1740, from a private collection was performed which highlighted the complexity of the sampling issue with a view to applying ^{14}C dating on different varnish layers.

Material history of the object

Little is known about the material history of this violin Pierre Saint-Paul, c.1740, private collection. Pierre Saint-Paul was a famous Parisian luthier who had a workshop in rue Saint André des arts in Paris since c.1742 (Vannes, 1932, p.312).

The original varnish was traditionally preserved as much as possible on bowed instruments despite numerous alterations-modifications-restorations over time (Chapter 1 – § 3.2.2). Since this violin was made in Paris during the mid-18th c., a shellac varnish is more likely expected (Chapter 1 – § 3.2.1).

Material characterization

- Identification of the varnish layers

A picture of the violin soundboard was taken under visible light (Vis) and under UV light at the Laboratoire du Musée de la musique (Figure 32). UV imagery revealed:

- (1) a lower layer of varnish
- (2) an upper layer of varnish (orange under UV light)
- (3) traces of glue (blue under UV light)

According to the expert report on violin making, the orange layer (2) is as a shellac-based varnish that might have been applied on the original varnish (1) since this upper layer is particularly visible on the used parts of the soundboard and also by the varnish runs left through the soundholes inside the violin. The glue (3) was identified as being of protein origin due to the blue color under UV light and might have been used to repair some fractures through time.

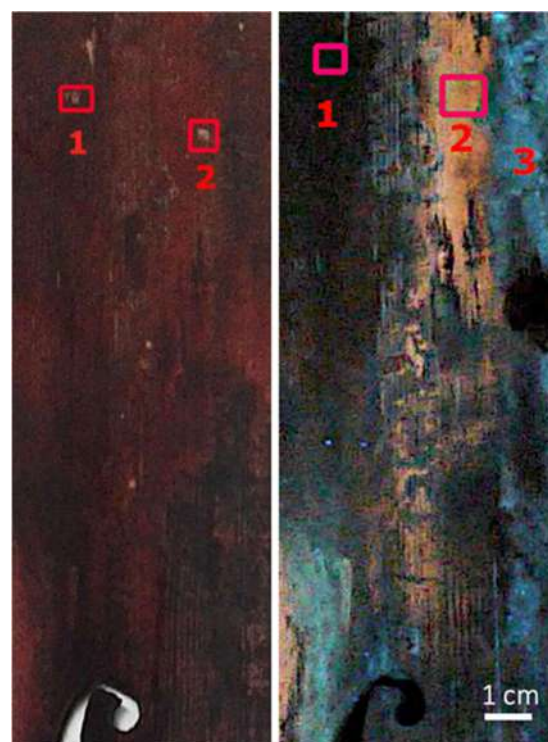


Figure 32. violin soundboard, Pierre Saint-Paul, c.1740 (left) under Vis light (right) under UV light.

- Sampling

Based on this initial expertise, the sampling locations were selected on a used part covered with the orange upper layer of shellac varnish under UV (2), on the brown layer under UV with the lower varnish (1), on the glue layer which is blue under UV (3) and on the wood from the rear side of the soundboard. Two other samples of shellac varnish (2) were also taken and numbered (2*) and (2**) (Appendix 4 – § 1).

In this case, mechanical sampling was performed using chisels commonly used by restorers at the Musée de la musique under a binocular microscope and UV light. The varnish was thin and brittle, producing powder under the chisel. The tip used by restorers to gather the varnish chips and powder using adhesive tape was proscribed due to the risk of ¹⁴C contamination.

- Contamination of varnish samples

ATR-FTIR analyses were performed on the samples previously selected using visual expertise and *in-situ* UV imagery (see Appendix 4 – § 1 for detailed spectra). The most likely assignments of some typical bands are briefly discussed in Appendix 4 – § 1.

The ATR-FTIR spectrum of the varnish (2*) shows differences between 2700 and 3600 cm⁻¹ compared to the expected peaks of shellac (Figure 33). The comparison with the ATR-FTIR spectrum of wood leads to the conclusion that the varnish layer was too thin to be sampled using common chisels and that the underlying wood contaminated the sample. However, the proximity to the animal glue applied punctually during repair interventions on the violin did not induce contamination (Figure 33).

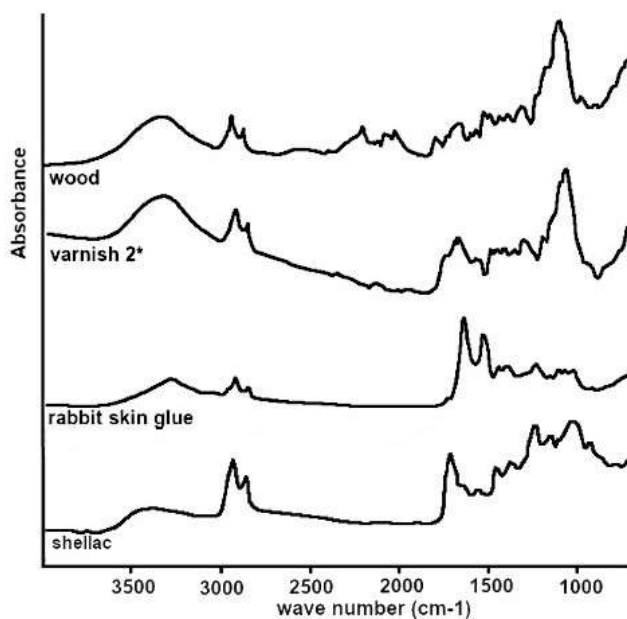
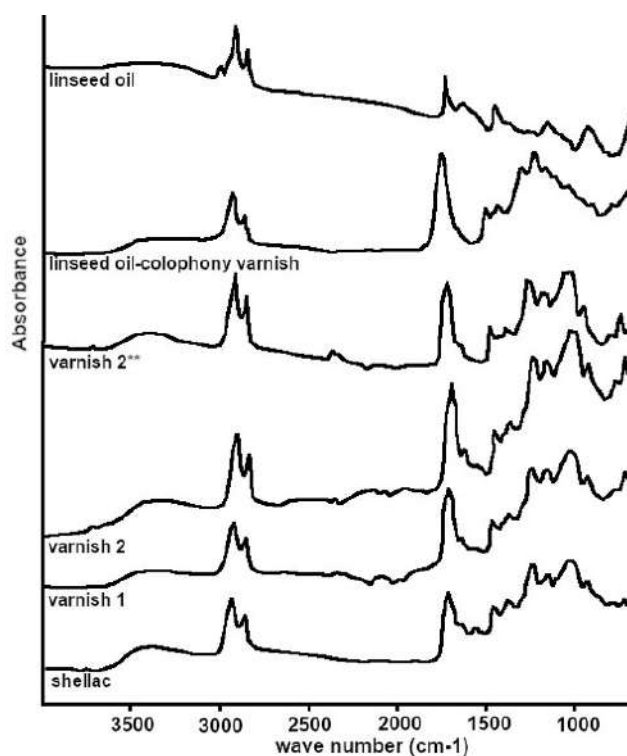


Figure 33. From the top to the bottom. ATR-FTIR spectrum of wood from the rear side of the soundboard; ATR-FTIR spectrum of varnish (2*); reference spectra of rabbit skin glue; reference spectra of shellac.

- Separating varnish (1) and varnish (2)?

ATR-FTIR spectra of the sampled varnish layers were compared with reference spectra of linseed oil, shellac, and a mixture of 10 g linseed oil with 10 g colophony in 2013 (Tirat, 2015). The comparison showed that the peaks of the samples matched a shellac-based composition (Figure 34). However, note that there are few peak differences between ATR-FTIR spectra of

varnishes with terpenoid resins (Daher, 2012). The most likely assignments of some typical bands are briefly discussed in [Appendix 4 – § 1](#).



*Figure 34. From top to bottom. ATR-FTIR spectrum of: linseed oil (*Old Holland); linseed oil-colophony varnish 10:10 prepared in 2013 (Tirat, 2015); varnish (2**); varnish 2; varnish 1; reference spectra of shellac.*

The case study of the violin Pierre Saint-Paul, c.1740 shows the complexity of isolating varnish layers for the application of ^{14}C dating. At this stage, it proved impossible to separate the successive layers using common chisels under UV light. For example, a sample was contaminated by the underlying wood. The contamination by glued materials cannot be excluded either, while traces of glue must be preferably avoided when applying ^{14}C dating ([Chapter 1, § 4.2](#)). Following these analyses, another sampling methodology was investigated through a survey among curators and scientists to limit contamination during the sampling.

3.2. Sampling using microchisels

After a survey among restorers, it was decided to use microchisels⁴⁶ to sample varnish layers following the Getty Institute protocol⁴⁷ (Heginbotham et al., 2008) also applied during the ELinC project in 2018⁴⁸ (Figure 35).

⁴⁶ Reference of the microchisels:

https://www.emsdiasum.com/microscopy/products/materials/micro_tools.aspx

⁴⁷ <https://www.youtube.com/watch?list=PL5ZJP2yRFa3aSNlyqUquOOPYpvx94Xv53&v=VNb2SRJ4sKs> (consulted on 2019/09/20, link sent by Arlen Heginbotham in a personal communication).

⁴⁸ Personal communication, Louise Decq. ELinC-European Lacquer in Context. BRAIN project (2012-2018) - Belgian Research Action through Interdisciplinary Networks, Belgian Science Policy Office.



Figure 35. Hard steel microchisels with different sizes of tool tip 0.120 mm, 0.25 mm, 0.5 mm and a handle sold separately.

The sampling missions were treated differently depending on whether they were field sampling or sampling performed at the Laboratoire du Musée de la musique. It is important to avoid carbon contamination during sampling, storage and transport of the samples to the laboratory. The use of carbon-free material is essential: aluminium paper, aluminium capsules, glass containers, etc. All tools and containers must be baked out at 450°C and kept under cover with burned aluminum foil during the whole process (Figure 38).

For field sampling, there are two sampling protocols:

- Samples of complete or incomplete varnish stratigraphies were taken under UV light and magnifying glasses using common chisels with new blades. They were wrapped in aluminium foil (pre-baked at 450°C). Then, the samples needed to be further treated in the laboratory to separate the varnish layers.
- The separation of early varnishes layer by layer was achieved directly during the field missions using microchisels, magnifying glasses and UV light. The subsamples were collected in glass tubes (glass shell vial 2 mL, Øxh 12x32 mm) pre-baked at 450°C.

For sampling in the laboratory:

- Varnish samples were taken layer by layer on a Heritage object in the laboratory using microchisels, magnifying glasses and UV light in the same way as in field missions. The intervention lasted around 1h30 per sampling for varnish sampling on a cello, Namy, 1773, Paris, private collection (Figure 36). However, varnish samples were also taken differently using microchisels under a binocular microscope and UV light. The intervention lasted around 3h to isolate a sample of red lacquer from a Chinese qin (n°inv.D.04224) (Figure 37). The subsamples were stored in glass tubes (Øxh 12x32 mm) pre-baked at 450°C (Figure 38e).
- Varnish stratigraphies collected on field missions were placed in clean aluminium capsules (Ø 14mm) and separated layer by layer using microchisels under a binocular microscope and UV light.



Figure 36. Varnish sampling on a cello, Namy, 1773, Paris, private collection using a microchisel 0.5 mm under UV light performed by Sebastiaan Kirsh. Video taken by Marie-Gabrielle Durier <https://youtu.be/Neen31VA8DQ>



Figure 37. Sampling of red lacquer on a Chinese qin D.04224 at the Musée de la musique, Paris. Sample and video taken by Marie-Gabrielle Durier. <https://youtu.be/izfl40391ck>

Here, varnish stratigraphies were sampled by:

- i- Isabelle Devergne on sleds under the supervision of Maria-Anne Privat at the Musée National de la Voiture et du Tourisme, Compiègne. Varnish stratigraphies were sampled using new blades of chisels provided by the LSCE. The interventions lasted around 1h per Heritage object studied.
- ii- Emanuele Marconi using microchisels and new blades of chisels on lacquered pieces of furniture under the supervision of Frédéric Dassas at the Louvre, Paris (around 1h per Heritage object)
- iii- Sebastiaan Kirsch using microchisels on two cellos, private collection at the Musée de la musique, Paris (around 1h30 per varnish sampling)
- iv- Louise Decq and Marie-Gabrielle Durier using microchisels on sleds under the supervision of Emile Van Binnebeke at the Royal Museums for Art and History, Brussels (around 1h30 per varnish sampling)
- v- Marie-Gabrielle Durier using microchisels under the supervision of Anne-Sophie Trivin at the Musée de la lutherie et de l'archèterie françaises, Mirecourt (around 1h30 per varnish sampling)

After each sampling intervention by specialized restorers, I was trained to be autonomous on mechanical sampling layer by layer for ^{14}C dating application on early varnishes.

3.3. Weight and identification of the sample

During field missions, the varnish layers separated layer by layer using microchisels were collected in glass tubes (shell vial $\varnothing \times h$ 12x32 mm) pre-baked at 450°C and weighed in a jewellery scale (G&G FC50 precision scale, 50 - 0.001 g \pm 0.002g recommended by P. Richardin, C2RMF) since the more suitable precision scales at the LSCE are not transportable. Varnish stratigraphies were weighed and wrapped in aluminium foil. The protected samples were then placed in plastic bags and boxes, respectively for varnish stratigraphies and glass tubes, and numbered according to a defined identification system MGD + n° (sample ID).

In the laboratory, the varnish stratigraphies were placed in aluminium capsules (\varnothing 14 mm) to prevent contamination by exogenous carbon elements. Then, they were divided layer by layer and weighed using the precision scale at the LSCE. The modalities of sample registration at the laboratory prior to ^{14}C measurements using ECHOMICADAS were still being defined at the beginning of the PhD study. Currently, they are completely established: each subsample from the same original sample MGD + n° (sample ID) has a same GifA + n° (chemistry ID). For instance, three layers of the same subdivided varnish stratigraphy are respectively numbered with a suffix: GifA + n° (chemistry ID .1), GifA + n° (chemistry ID .2), GifA + n° (chemistry ID .3).

4. Radiocarbon dating protocols

The whole process for applying ^{14}C dating on Heritage materials comprises several steps:

- sampling on field missions in museums to sample: i- isolated varnish layers using microchisels or ii- varnish stratigraphy fragments on the Heritage objects
- sampling in the laboratory to sample varnishes layer by layer on the Heritage object or to separate the layers of varnish sampled during field missions
- additional (non-destructive) analyses on micro-samples
- chemical treatments to remove contaminants or to extract the fraction of interest
- conversion of the samples into CO_2 , by combustion or thermal decomposition
- reduction of the extracted CO_2 to graphite C for samples with the highest amount of carbon
- measurements of ^{14}C contents by ECHOMICADAS

4.1. Specific chemical treatments

Chemical glasses and protective aluminium foils were previously baked out at 450 °C during 6 hours, making them carbon-free. All chemicals were of ultrapure quality, and water was ultrapure (MilliQ grade).

4.1.1. Choice of protocol and material

The samples were treated according to their nature (wood, varnish, pigment, ...), their physical state (powder, chips), the expected contamination to be removed, and their state of preservation. Adaptations were made during the study notably to take into account the physical state of the sample (e.g. powder) which complicated the chemical treatments.

The choice of containers to perform chemical treatments also depends on the sample including its size and the anticipated treatments. It can be a thick glass centrifuge tube, a glass tube (vial) or a glass tube especially modified for very small samples. The centrifuge tube is used for large samples (> 2mg), the glass tubes (vials) are used for samples requiring solvent extractions, and the narrow-bottomed glass tube for the smallest samples (Figure 38).

The specific narrow-bottomed glass tube was used to eliminate the transfer step of the sample after the chemical treatments and to reduce the associated material losses. After solvent drying, the sample is concentrated in the bottom of the tube with a very small amount of water; and a clean metal rod is inserted. The tube, water, sample and rod are frozen in liquid nitrogen. The surface of the glass nose is then warmed up to detach the ice cube containing the sample which is then removed with the rod. It is deposited at the bottom of a microline tube for combustion. The sample is finally dried in the vacuum oven or freeze-dryer. This system is called "the fishing rod".

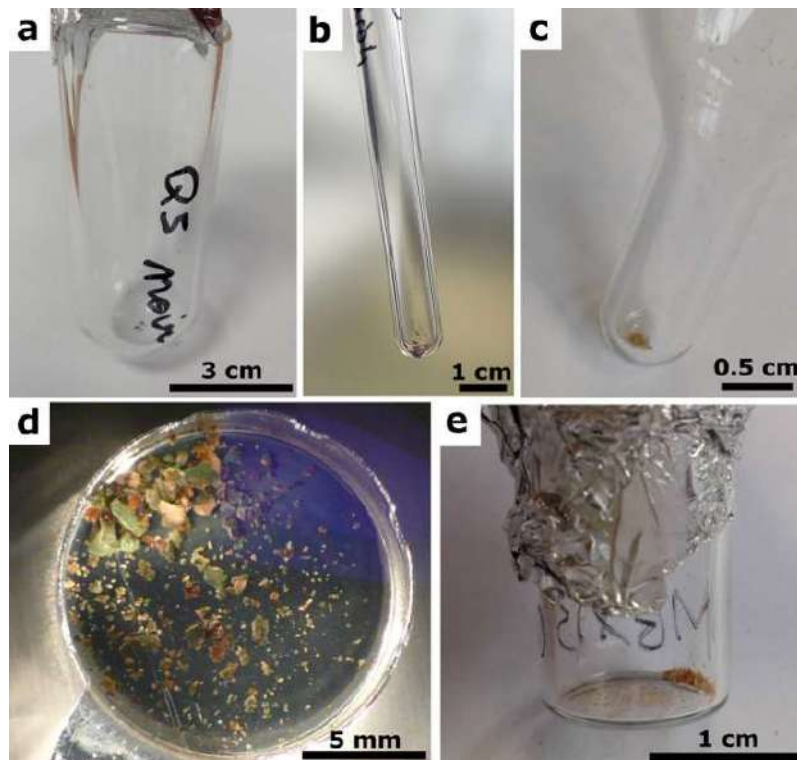


Figure 38. a) glass centrifuge tube, b) glass microline tube, c) narrow-bottomed glass tube, d) aluminium capsule, e) glass tube (vial)

4.1.2. wood treatment

The classical treatment for wood samples derived from the AAA chemical protocol (van Klinken and Hedges, 1998) using alternately hydrochloric acid and sodium hydroxide base (Figure 39):

- 1) HCl 0.5 M at room temperature. After 30 min, rinsing with ultrapure water until pH=5. A Pasteur pipette is used to add and remove water.
- 2) NaOH 0.1 M at room temperature. If any reaction occurs, the sample is rinsed after 30 min with ultrapure hot water until pH=5.
- 3) HCl 0.5 M at room temperature. After 30 min, the sample is rinsed with ultrapure water until pH=5.
- 4) the sample is freeze-dried or dried in a vacuum oven at 45°C.

Note that if there are any chemical reactions at step 1 or 2, e.g. a change in colour of the solution or the sample, the solution (HCl or NaOH) is removed and replaced by a fresh one for another 30min. For example, the acid solution became pink for the treatment of a sample from the bird bridge of an Indian vina made of *Dalbergia latifolia* or "Indian rosewood" (E.1444, Musée de la musique collection) (Durier et al., 2019a) (Figure 39).



Figure 39. AAA chemical protocol classically applied on wood and charcoal ; HCl 0.5 M at room temperature (left) ; hot rinsing at 80 °C of the samples in glass tubes (right) (van Klinken and Hedges, 1998)

4.1.3. individual layers of varnishes

The chemical preparation here consisted essentially of removing the dust or traces of the underlying preparation layers (e.g. lead white). Hence, we only applied acid pre-treatments. This preparation was performed in narrow-bottomed glass tubes.

Nevertheless, the last sampling step done in the laboratory to individualize the varnish layers often produces powder or very light splinters. This kind of sample floats inhomogeneously in acid or water. The chemistry is not optimal and the use of the Pasteur pipette for the rinsing step is therefore complicated. We therefore modified the protocol to overcome this problem. Instead of rinsing by adding and removing water with a Pasteur pipette, the water was removed in the freeze dryer. We experimented two rinses with a volume of water equivalent to 3-4 times the volume of acid, which proved sufficient to reach a pH=5. As a precaution, the operation was performed 3 times.

- 1) HCl 0.5 M at room temperature. After 30 min, water addition up to the "nose" height.
- 2) liquid nitrogen freezing and freeze-drying
- 3) 3 times: water addition up to the "nose" height, liquid nitrogen freezing and freeze-drying
- 4) transfer into quartz tube for micro-line using the "fishing rod" system
- 5) the sample is freeze-dried or dried in vacuum oven at 45°C

4.1.4. lead white

To remove any residue of lead white, including geological carbonate, an acid treatment with HCl at 0.5N or 1N is sufficient. Acetic acid may be enough to solubilize lead oxide (chemistry handbook) but strong acid is recommended to remove both lead oxide and limestone residues.

The organic fraction of lead white is extracted by thermal decomposition at 300°C according to the recommendations of Messenger et al. (2020). A higher temperature plateau evolves carbon from geological carbonates (limestone) that can be used or mixed with lead white in preparation layers. The [0-300°C] is intended to release only carbon that is contemporaneous of the lead white manufacture. As this carbon fraction is obtained by soft carbonation, it is expected to be thermally decomposed at a lower temperature than geological carbonate.

4.1.5. music instrument strings

The challenge was to define a chemical protocol, based on solvent use, capable of removing all of the colophony and fingerprints (possibly younger than the string) without adding carbon contamination by the solvents.

Several chemical treatments were tested to remove the dirty surface with dust and sticky colophony

- protocol n°1: AAA treatment (§ 4.1.2) was eliminated from the start. It induces material loss (protein hydrolysis) and dislocation of the twisted fibers of the string and is unable to fully efficiently remove all the colophony.
- protocol n° 2: three baths of dichloromethane (CH₂Cl₂, DCM) for 10 min in an ultrasonic bath, followed by a drying time of 24 h (thereafter "DCM x 3")
- protocol n° 3: three baths of dichloromethane/methanol (CH₃OH, MeOH) 1:1 followed by water rinsing, acetone ((CH₃)₂O, Ac) rinsing, and water rinsing (thereafter "DCM/MeOH/Ac")

For each string, we applied the DCM treatment twice and the DCM/MeOH/Ac treatment once. Solvent from baths that were used to dissolve colophony on gut strings was analysed by GC-MS to check the presence or not of colophony. GC-MS analyses of the solvent from the third bath showed that molecules from the gut strings (proteins) began to be hydrolyzed. The sample size of the gut strings was enough for ¹⁴C dating using the solid source (AGE3) (see [methodological part, Chapter 3 – § 4.2](#)).

This protocol could be extended to treat other Heritage materials impregnated with colophony or fingerprints.

4.2. Conversion to CO₂ on micro-line, EA-GIS or AGE (and reduction to C)

The chemistry step to withdraw carbon contaminants is followed by a final step of carbon conversion and purification before injection in the mass spectrometer ECHOMICADAS. The injection way is chosen depends on the sample size and on the nature of the sample: micro-line + cracking-GIS, EA-GIS or AGE (Table 13). A description of the micro-line system is given in [Appendix 2 – § 2.2](#) (Figure 40). A description of cracking-GIS, EA-GIS and AGE3 can be found in Ruff et al., 2007, 2010; Wacker et al., 2010 respectively.

The lead white is thermally decomposed on the micro-line according to the temperature step of Messenger, 2020.

Table 13 : how to choose between the micro-line, EA-GIS and AGE3 ? ... according to the sample mass

mass		20	30	40	...	150	...	250	...	400	...	600	...	1400	...
mass	µg C	20	30	40	...	150	...	250	...	400	...	600	...	1400	...
	µg varnishes [70%wt C]	25	38	50
	µg wood [50%wt C]	40	60	80	...	75	...	125	...	800	...	1000	...	1300	...
Reliable measurement															
µ ligne *	1 tube = 1 measurement														
	2 tubes**= 2 measurements														
	3 tubes ***= 3 measurements														
	4 tubes ©= 4 measurements														
EA-GIS (Δ)	1 capsule														
	2 capsules=2 measurements														
	3 capsules=3 measurements														
	4 capsules=4 measurements														
AGE3	AGE 1 target														
	2 targets														
<p>* : reserved for samples for which a "pre" cannot be made, samples smaller than 60 µg C or samples with unknown carbon content</p> <p>** : to avoid the loss of a valuable sample, 2 tubes are preferable to one in case of glass breakage</p> <p>*** and © : only for very valuable samples, very old samples (>25kyr) or very precise measurement</p> <p>(Δ) : use if the C content is known, with a "pre" (before the sample or a standard) and for samples with a weight > 40 µg C</p>															

Organic samples are directed to the micro-line + cracking-GIS, EA-GIS or AGE3 according to the following rules:

- the carbon content is not known and we were unable to evaluate it independently → micro-line + cracking-GIS
- the carbon content is known (or estimated) and the amount of expected carbon is less than 600 μ gC → EA-GIS
- the carbon content is known (or estimated) and the amount of expected carbon is more than 600 μ gC → AGE3



Figure 40. micro-line (see description of the microline in Appendix 2 – § 2.2).

4.2.1. Physical measurements

The accelerator mass spectrometer, ECHoMICADAS, was used to measure the ^{14}C activity of each sample (Synal et al., 2007; Tisnérat-Laborde et al., 2015) that was directly injected via the GIS interface for gaseous samples (Ruff et al., 2010). The results are expressed in $F^{14}\text{C}$ (Reimer et al. 2004) and BP years (Stuiver and Polach, 1977).

4.2.2. Bayesian statistics using OxCal

Probability distributions of the calibrated ages are then generated using OxCal software, v. 4.4 (Bronk Ramsey, 2009) from the IntCal20 calibration curve (Reimer et al., 2020).

5. Known oil-colophony mixture: ^{14}C dating on bulk varnishes

The complexity of the chemical constitution of early linseed oil/colophony varnishes that also underwent modifications through time was expected to be one of the obstacles for the application of ^{14}C dating. A first issue was to evaluate the impact of drying linseed oil/colophony mixtures and their ageing on ^{14}C dating compared to their raw ingredients. Although we initially postulated that no impact would be measured, we decided to carry out experiments on lab-prepared mixtures to verify the relevance of performing ^{14}C dating at “bulk” level. ^{14}C dating at molecular level was not investigated further due to the difficulties in retrieving the original molecules of original ingredients before the varnish making as previously reported.

Linseed oil/colophony mixtures were prepared and analysed using radiocarbon dating to compare the ^{14}C contribution of each fresh ingredient (Table 14) to dry varnishes (Table 15). Linseed oil and colophony were chosen with a significant age difference: i- an ingredient with a high ^{14}C content (colophony MGD21 [®]Laverdure, Chinese violin colophony MGD22 [®]Tiqin Songxiang, MGD38 linseed oil Canada) produced during the bomb peak, and ii- the other ingredient with a lower ^{14}C content (MGD25 violin colophony provided by Denis Caban's workshop, MGD31 linseed oil [®]Old-Holland Classic Colours) (Table 14).

Table 14. ¹⁴C results of colophony and linseed oils used to produce artificial linseed oil-colophony varnishes using AGE3 and the ECHoMICADAS solid source. Calibration was done with IntCal20 (Reimer et al. 2020) and the Bomb21 (NH1, Hua et al. 2021) calibrations, thanks to the OxCal v4.4 software (Bronk Ramsey 2009).

sample ID				Chemistry	Mass [µgC]	raw data		processed data			
Sample	MGD ID	Chemistry ID	measurement ID			F ¹⁴ C	±	Acomb / An	F ¹⁴ C	± [**]	IntCal20 & Bomb21 cal. ranges [AD] (95.3% proba)
linseed oil	MGD38	GifA20175.1	ECHo-3392.1	-	125 [*]	1.8179	0.0136	127.9 /50.0	1.7817	0.0026	[1963.4 – 1963.6] (3.3) [1964.8 – 1965.9] (92.3)
		GifA20175.2	ECHo-3160.2	-	986	1.7834	0.0037				
		GifA20175.3	ECHo-3160.3	-	984	1.7800	0.0036				
linseed oil	MGD31	GifA19376.2	ECHo-3161.2	-	993	1.0303	0.0023	66.9 /50.0	1.0276	0.0038	[1955.6 – 1956.3] (13.5) [2012.9 – 2016.1] (81.9)
		GifA19376.3	ECHo-3161.3	-	998	1.0249	0.0023				
colophony	MGD25	GifA19370.2	ECHo-3153.2	-	998	0.9736	0.0022	125.2 /50.0	0.9725	0.0016	[1647.1 - 1670.8] (42.0%) [1779.9 - 1797.9] (42.4%) [1942.4 - 1943.9] (0.6%) [1944.4 - 1947.6] (1.4%) [1948.1 - 1953.1] (9.1%)
		GifA19370.3	ECHo-3153.3	-	991	0.9714	0.0022				
colophony	MGD21	GifA19366.2	ECHo-3159.2	-	997	1.2907	0.0028	145.1 /50.0	1.2872	0.0050	[1959.5 – 1959.6] (1.5) [1961.9 – 1962.4] (24.8) [1979.6 – 1980.8] (69.2)
		GifA19366.3	ECHo-3159.3	-	998	1.2836	0.0028				
colophony	MGD22	GifA19367.2	ECHo-3163.2	-	993	1.4703	0.0031	121.6 /50.0	1.4688	0.0022	[1963.0 – 1963.3] (7.9) [1972.5 – 1973.1] (83.9) [1973.5 – 1973.8] (3.6)
		GifA19367.3	ECHo-3163.3	-	998	1.4673	0.0031				

[*] note that 125µg of carbon is far below the regular range for AGE3. This value is not taken into account in the combination.

[**] max between the Chi2 reduced error and the standard deviation of the individual values

Linseed oil/colophony mixtures were prepared in the laboratory based on the experiments described by Tirat (2015, p.66, p.107)(Figure 41). The proportion 70:30 for linseed oil and colophony was chosen according to the traditional recipes of the 17th c. Italian violin varnishes (Echard, 2010)(Chapter 1 – § 3.2.3).



Figure 41. Preparation of linseed oil colophony varnishes for ¹⁴C dating and Sr isotopy measurements

For the production of the lab-varnish MGD47, the weighed mass of the linseed oil sample MGD31 was 825.7 mg and that of the colophony sample MGD21 400.8 mg. The initial temperature of the hot plate was 50 °C, followed by a 3°C/min ramp to 230 °C to heat first the linseed oil, followed by the addition of colophony; the hot plate was held at 230 °C for a further 80 min.

For the production of the lab-varnish MGD45, the weighed mass of the linseed oil sample MGD38 was 849.5 mg and that of the colophony sample MGD25 350.3 mg. The initial temperature of the hot plate was 50 °C, followed by a 6°C/min ramp to 230 °C to heat first the linseed oil, followed by the addition of colophony; the hot plate was held at 230 °C for a further 80 min. The temperature ramp was faster for the linseed oil sample MGD38 because this oil was not fresh but dated from the 1960s.

The Chinese violin colophony MGD22 Tiqin Songxiang was not used to produce a lab-varnish, but it was kept in storage due to the limited amount available.

Table 15. ^{14}C results of artificial linseed oil-colophony varnishes using AGE3 and the ECHO MICADAS solid source. Calibration was done with IntCal20 (Reimer et al. 2020) and the Bomb21 (NH1, Hua et al. 2021) calibrations thanks to the OxCal v4.4 software (Bronk Ramsey 2009).

sample ID				Chemistry	Mass [μgC]	raw data		processed data			
Sample	MGD ID	Chemistry ID	measurement ID			$F^{14}\text{C}$	\pm	Acomb / An	$F^{14}\text{C}$	\pm [*]	IntCal20 & Bomb21 cal. ranges [AD] (95.3% proba)
MGD38 linseed oil and MGD25 colophony	MGD45	GifA20471.1	ECHO-3900.1	-	989	1.0910	0.0035	114.8 /40.8	1.0937	0.0028	[1957.6 – 1958.0] (9.3) [1999.0 – 2001.1] (83.2) [2001.5 – 2001.8] (3.0)
		GifA20471.2	ECHO-3900.2	-	995	1.0934	0.0034				
		GifA20471.3	ECHO-3900.3	-	991	1.0965	0.0034				
MGD31 linseed oil and MGD21 colophony	MGD47	GifA20472.1	ECHO-3901.1	-	993	1.5572	0.0046	152.4 /40.8	1.5543	0.0027	[1969.1 – 1970.9] (94.1) [1971.4 – 1971.6] (1.3)
		GifA20472.2	ECHO-3901.2	-	1000	1.5523	0.0046				
		GifA20472.3	ECHO-3901.3	-	993	1.5534	0.0046				

[*]max between the Chi2 reduced error and the standard deviation of the individual values

Table 16. Composition of the varnishes prepared in the laboratory. $F^{14}C_{th}$ is the theoretical value based on the metrology and the $F^{14}C$ of ingredients and $F^{14}C_{exp}$ is the value we measured.

Colophony				Linseed oil				Varnish			% oil/(colophony+oil)	
sample ID	C content [%wt] [*]	mass [mg]	$F^{14}C$	sample ID	C content [%wt] [*]	mass (mg)	$F^{14}C$	sample ID	($F^{14}C$)th	($F^{14}C$)exp	% th	% exp
MGD25	76.30 ±0.31	350.3 ±0.1	0.9725 ±0.0016	MGD38	80.31 ±0.43	849.5 ±0.1	1.7817 ±0.0026	MGD45	1.512 ±0.018	1.5543 ±0.0027	71.9 ± 0.7	71.9 ± 0.9
MGD21	74.04 ±0.29	400.8 ±0.1	1.2872 ±0.0050	MGD31	77.38 ±0.53	825.7 ±0.1	1.0276 ±0.0038	MGD47	1.124 ±0.020	1.0937 ±0.0028	68.3 ± 0.8	74.6 ± 2.6

[*] carbon content is determined on EA based on duplicate measurements

The experiment described here was used to compare the $F^{14}C$ values of the ingredients and the experimental $F^{14}C$ of the dried and aged varnish films with the theoretical $F^{14}C$ values of the varnishes. The theoretical $F^{14}C$ values of the varnishes were calculated based on a mixed rule to verify the experimental effect of evaporation or oxidation on ^{14}C dating:

$$F^{14}C(\text{varnish}) = \frac{\%C \times m(\text{linseed oil}) \times F^{14}C(\text{linseed oil}) + \%C \times m(\text{colophony}) \times F^{14}C(\text{colophony})}{\%C \times m(\text{linseed oil}) + \%C \times m(\text{colophony})}$$

According to the experimental $(F^{14}C)_{\text{exp}}$ measured on the MGD45 and MGD47 varnishes compared with the theoretical $(F^{14}C)_{\text{th}}$ calculated based on the $F^{14}C$, mass and carbon content values of the ingredients, we determined that the $F^{14}C$ of linseed oil has a greater impact than expected on the final $F^{14}C$ of the varnishes after the baking and drying processes (Figure 31).

This could be due to the ratio of long molecules which is higher in linseed oil than in colophony. The carbon content of the long (i.e. heavy) molecules is higher than that of the short (i.e. light) molecules and heating favors the evaporation of the short molecules. By favoring the evaporation of the molecules with a relatively low carbon content, the varnish making leads to an increase in the molar mass of linseed oil. Consequently, the contribution of linseed oil carbon increases throughout the evaporation process.

Based on current knowledge on early practices, we assumed that organic binders (natural oils and resins) were contemporaneous of the varnish making ([Chapter 1 – § 3.4](#)). Even if one can argue that natural resins could have been stored several years, the dating of linseed oil/colophony varnishes is more consistent with the dating of linseed oil which was used fresh for practical reasons, since linseed oil loses its fluidity with ageing and storage.

6. Historical, material and dating analyses object by object

Our research essentially concerns radiocarbon dating applied to historical varnishes dated from the modern period. ^{14}C dating was performed at “bulk” scale because chemical separation tests using GC-MS at the LSCE were inconclusive ([Appendix 1](#)). The interpretation of the ^{14}C results on “bulk” varnishes needed to be accurately cross-linked with information on the material history, the localization and material characterization analyses of the samples for each object. Sampling always depends on the objects and cross-sections were taken from carefully selected locations thanks to museum experts completed with the identification of materials: what is the original stratigraphy? How was it made?

So, for the sake of clarity, this chapter will not follow a classical plan, and the results will be presented object by object according to their corpus collection and their level of documentation.

6.1. Overview of the material corpus

Our research initially concerns radiocarbon dating applied to linseed oil/colophony varnishes dated preferentially from the early 18th c. We try to avoid the period between 1730 and 1770. Indeed, the calibration curves lead to more reliable values in the following range of dates during the modern period: [1600 - 1730] or [1770 - 1810]. The experimental program involves early varnishes from modern musical instruments, furniture and sleds ([see material corpus with contacts in Appendix 3](#)) kept in:

- Private collections
- Public collections

¹⁴C dating measurements were also conducted on gut strings of stringed instruments which are rich in evidence of historical (musical) use practices.

A summary is given in Table 35.

6.2. Musical instruments

6.2.1. Cello, head carved by “Lafille”, 18th c.

Material history of the object

A cello from the atelier N. Perrin (private collection, Paris) has a head which was carved by “Lafille”, Paris, 18th c. with five daisies initially designed for 5 pegs of a viola.

Sampling and material characterization

Mechanical sampling on the original varnish of the carved head was carried out using a 0.5 mm micro-chisel under UV light, avoiding dust in the cavities of the sculpture. The original varnish layer is yellow under UV light, indicative of a linseed oil-colophony varnish.

- o Sample MGD100

This varnish sample comprises: i- varnish chips taken on a carved flower, and ii- varnish chips taken on an undecorated part on the left side of the scroll. The total surface of the sampled varnish corresponds to a minimum previously calculated (around 2x2 mm²) which was theoretically estimated as necessary for applying ¹⁴C dating (Figure 42).

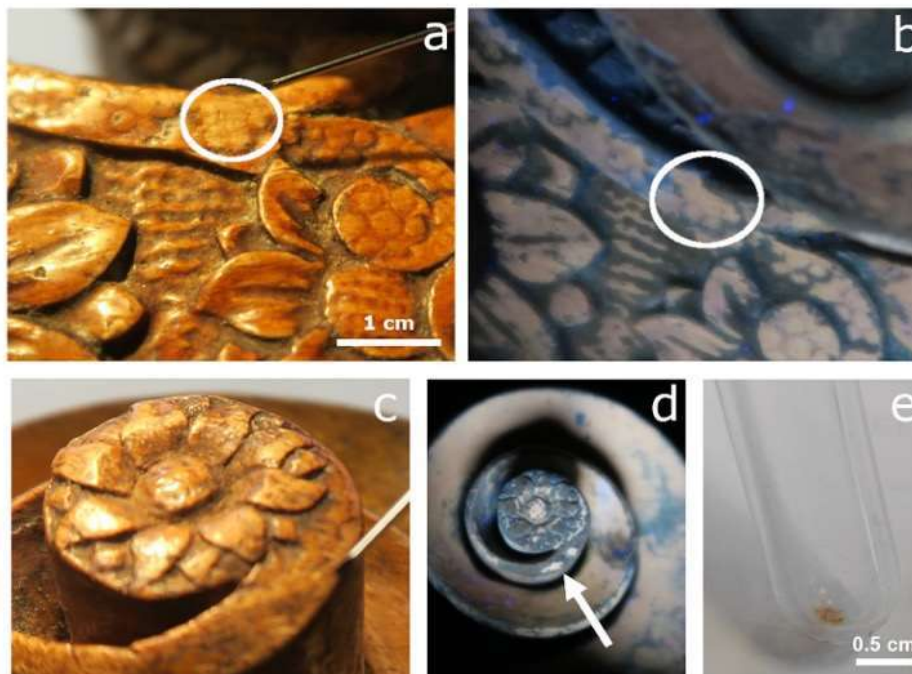


Figure 42. a) sampling 1 of the original varnish on a miniature daisy, b) picture of sampling 1 under UV light, c) sampling 2 of the original varnish on the cello scroll, d) picture of sampling 2 under UV light, e) picture of the complete varnish sample MGD100 that includes 1 and 2 in a glass tube for ¹⁴C dating.

- o Sample MGD101

This varnish sample comprises varnish chips taken on two flowers on the right side of the scroll of the cello head (Figure 43).

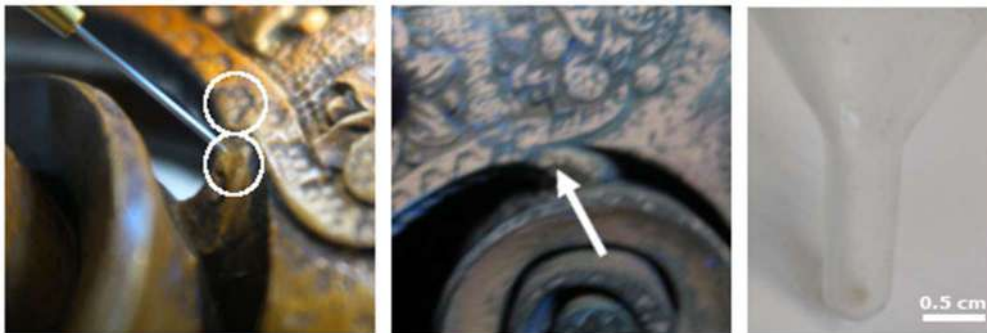


Figure 43. (from left to right) sampling MGD101 of the original varnish on two miniature daisies, picture of sampling 2 under UV light, picture of the varnish sample in a glass tube for ¹⁴C dating.

Radiocarbon results

Sample MGD100 of varnish on the head of the cello (18th c., Paris) gave the interval: [1529 – ...] and sample MGD101 gave the interval [1303 – ...] (Figure 44, Table 17). After using the “combine” option in Oxcal, the Acomb was 73%. The inconclusive results are a consequence of the low masses of carbon obtained: 48 µgC for MGD100 and 18 µgC for MGD101 that yielded for high measurement uncertainties are high with values of 0.010 and 0.019, respectively (Table 17).

Table 17. ¹⁴C results on the chips of varnish of the head of the cello carved by "Lafille", circa 18th c. (private collection). The EA-GIS interface was used to produce and introduce the CO₂ into the ECHOmicADAS gas source. Calibration was done with IntCal20 (Reimer et al. 2020) thanks to the OxCal v4.4 software (Bronk Ramsey 2009).

sample ID				Chemistry	Mass [µgC]	raw data				processed data
Instrument	MGD ID	chemistry ID	measurement ID			F ¹⁴ C	±	year [BP]	±	IntCal20 cal. ranges [AD] (95.4%)
Lafille cello	MGD100	GifA20232	ECHO-3482.1.1	A	48	0.981	0.010	150	80	[1529 – ...]
	MGD101	GifA20233	ECHO-3483.1.1	A	18	0.955	0.019	370	160	[1303 – ...]

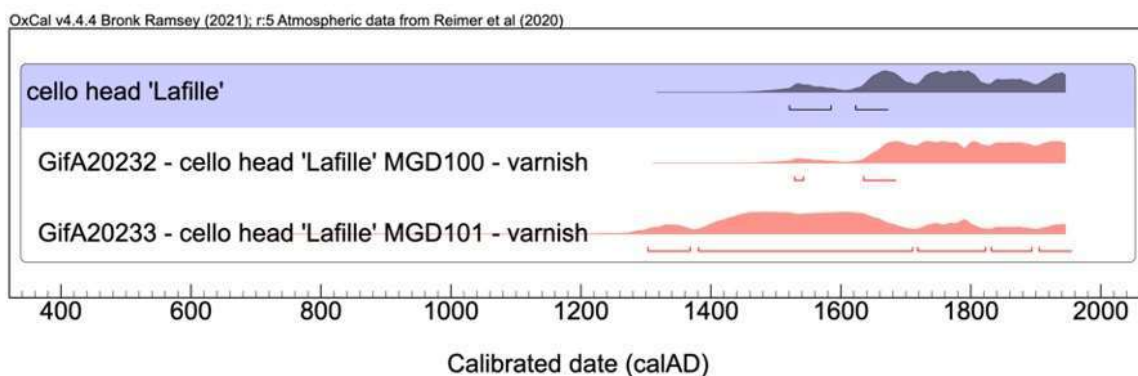


Figure 44. Calibrated range of dates using IntCal20 on original varnish of the head of the cello carved by "Lafille", circa 18th c. (private collection) (Reimer et al., 2020)

6.2.2. Cello, Namy, 1773

Material history of the object

The cello, Namy, 1773, Paris comes from the atelier N. Perrin (private collection, Paris). Jean-Théodore Namy (c.1750-1808) was a Parisian violin maker and skilful restorer with a workshop at Mrs Salomon's in 1772.

Material characterization

Two successive layers of varnish were detected under UV light, i.e. a yellowish layer identified as the original oil-based varnish and an orange layer made of shellac. Based on restorer expertise and UV imagery, two sampling locations were chosen on the original varnish layer. The chips of varnish were taken using a 0.5 mm microchisel and collected in a glass tube for ^{14}C measurements (Figure 45).

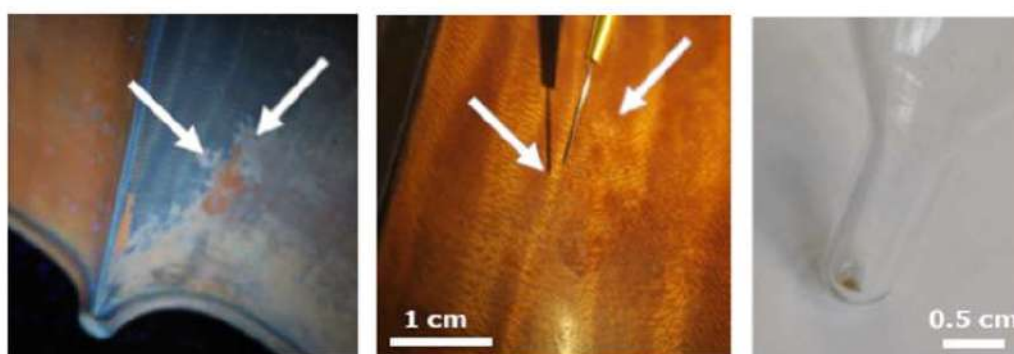


Figure 45. (from left to right) Picture of the sampling location of the original varnish layer which is yellow under UV light, picture of the sampling MGD102 with a 0.5 mm microchisel under visible light, picture of the varnish sample in a glass tube for ^{14}C dating.

Radiocarbon results

The range of dates obtained using ^{14}C measurements on the chips of original varnish was [1524– ...] (Table 18, Figure 46). Once more the measurement uncertainty is high with values of 0.020 (> 0.007, the typical error for masses higher than 100 μgC) due to the too small size of the sample, i.e. 16 μgC (Table 18).

Table 18. ^{14}C results on the chips of varnish of the cello, Namy, 1773 (private collection). The EA-GIS interface was used to produce and introduce the CO_2 into the ECHO MICADAS gas source. Calibration was done with IntCal20 (Reimer et al. 2020) thanks to the OxCal v4.4 software (Bronk Ramsey 2009).

sample ID				Chemistry	Mass [μgC]	raw data				processed data
Instrument	MGD ID	Chemistry ID	measurement ID			F^{14}C	\pm	year [BP]	\pm	IntCal20 cal. ranges [AD] (95.4%)
Cello, Namy, 1773	MGD102	GifA20234	ECHO-3484.1.1	A	16	1.015	0.020	120	170	[1524 – ...]

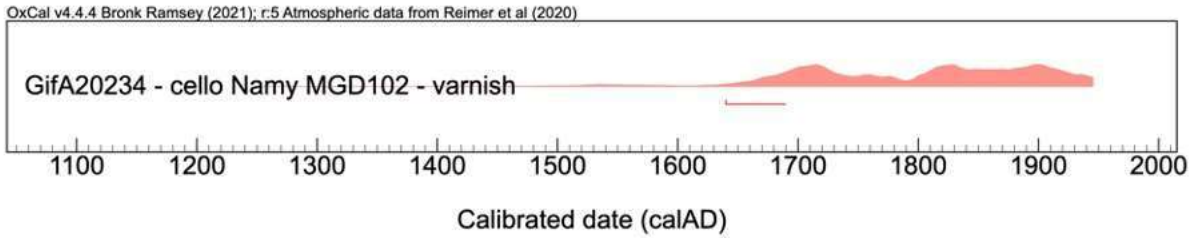


Figure 46. Calibrated range of dates using IntCal20 on original varnish of the cello, Namy, 1773 (private collection) (Reimer et al., 2020)

6.2.3. Baroque violin, anonymous, inv. 1993.1.1, coll. Musée de Mirecourt

Material history of the object

Little is known about the material history of this baroque violin, unknown, n° inv. 1993.1.1 kept at the Musée de Mirecourt. This violin was considered to be the oldest in the collection and was assumedly dated between 1699 and 1710. The dismantled soundboard is made of two pieces of spruce wood with a repair made of a piece of maple. The varnish layer is thought to be original and has a pale-yellow colour under visible light and a pale-orange colour under UV light (Figure 47). Here, varnish layers were sampled for ^{14}C dating and physico-chemical characterization. ^{14}C dating results were compared to dendrochronological tests.



Figure 47. (from left to right) picture of the baroque violin, anonymous, Mirecourt, n° inv. 1993.1.1 without the soundboard (61x20.2x9cm); picture of the soundboard under visible light taken by Claude Philippot © musée de Mirecourt ; picture under UV light of the soundboard with the distribution of the light-orange varnish layer. <http://www.musee-lutherie-mirecourt.fr/index.php?rub=collections&idmenu=2&limite=60>

Dendrochronology

A dendrochronological study was performed based on digital pictures showing that the soundboard dates from c.1780 using a formula reported by Baillie and Pilcher (1973) and references from the International Tree-Ring Data-Bank (ITRDB)⁴⁹. The growth direction of the

⁴⁹ Personal communication by Peter Ratcliff to Sebastian Kirsch

rings is from the edges towards the centre joint of the two pieces of spruce wood with 100 rings on the bass side, and 93 rings on the treble side (here, the last ring is dated from 1773 and the first visible ring is from 1680). Both halves may have come from the same tree due to excellent correlations.

After combining the data, good correlations were established mostly with French instruments built in the late 18th c. such as: violin, Vincenzo Panormo (?), Paris, c.1780; double bass, C.F. Landolfi, Mirecourt (?), c.1770; violin, Cacassi (?), France, mid-18th century (?); violin, Joseph Bassot, 1764, etc. According to Peter Ratcliff, the cross-dating results provide a year of 1778 for the last ring of the bass side and 1773 for the last ring of the treble side, which suggests a making period c.1780. Stored wood dating from the late 18th c. could possibly have been re-used in the early 19th c.

Results provided by Ratcliff also suggest that the region of tree growth was the Bavarian Forest, but comparison with databases with series from the Black Forest and the Vosges in France would require further research. It is currently assumed that French corporations during the pre-Revolution period had specific sources of wood which changed completely after their dissolution.

Sampling location

A picture of the rear side of the soundboard of the violin was taken under UV light at the Laboratoire du Musée de la Musique (Figure 48) showing:

- i- runs of a varnish layer through the soundholes in light orange under UV light
- ii- traces of glue in blue under UV light



Figure 48. (a) Rear side of the soundboard of the baroque violin, anonymous, Mirecourt, n° inv. 1993.1.1 (61x20.2x9cm) under UV light (14/04/2021, Musée de la musique)

Two varnish samples for ¹⁴C dating were taken on the varnish runs under the violin soundholes: sample MGD149 under the left soundhole (treble side) and sample MGD150 under the right soundhole (bass side) (Figure 49). Two varnish chips IR1 and IR2 were taken separately for material characterization using ATR-FTIR in order to identify the organic composition of the varnish respectively near MGD149 and MGD150. The samples were taken with a microchisel under a binocular loupe. The sample weight is about 1 mg for MGD149 and 2 mg for MGD150 (Figure 50, Figure 51).

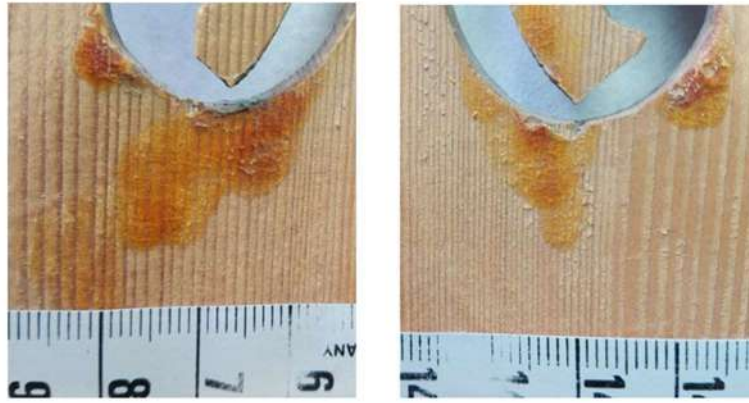


Figure 49. From left to right: MGD149 sample under the left soundhole (treble side) and MGD150 sample under the right soundhole (bass side) of the violin, anonymous, Mirecourt, n° inv. 1993.1.1

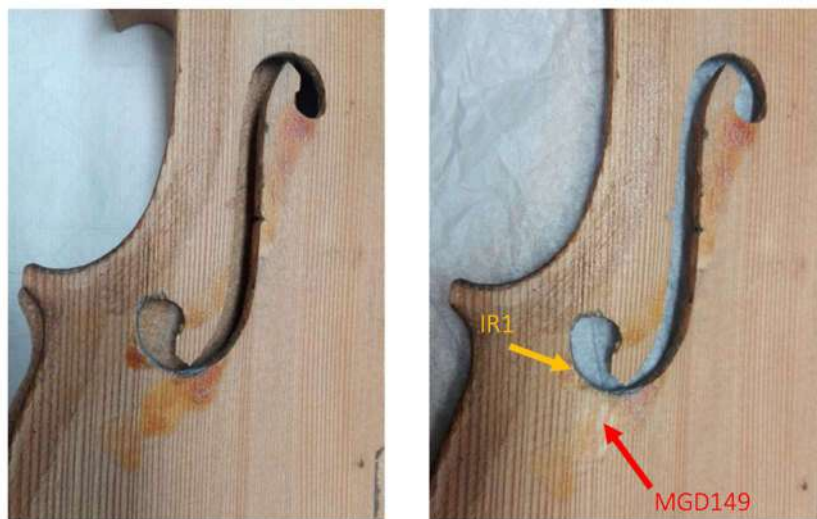


Figure 50. Pictures before (left) and after (right) the sampling of the MGD149 sample for ^{14}C dating and the IR1 varnish chip for ATR-FTIR analyses

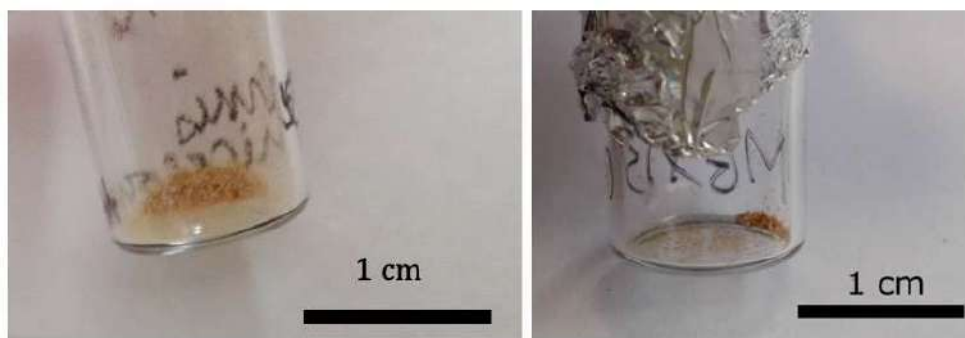


Figure 51. (from left to right) Varnish sample MGD149 for ^{14}C dating; varnish sample MGD150 for ^{14}C dating

Material characterization

After ATR-FTIR analyses, the spectra obtained for the IR1 varnish chip (blue) and the IR2 varnish chip (green) correspond to the reference of shellac [®]Sennelier (red) (Figure 52).

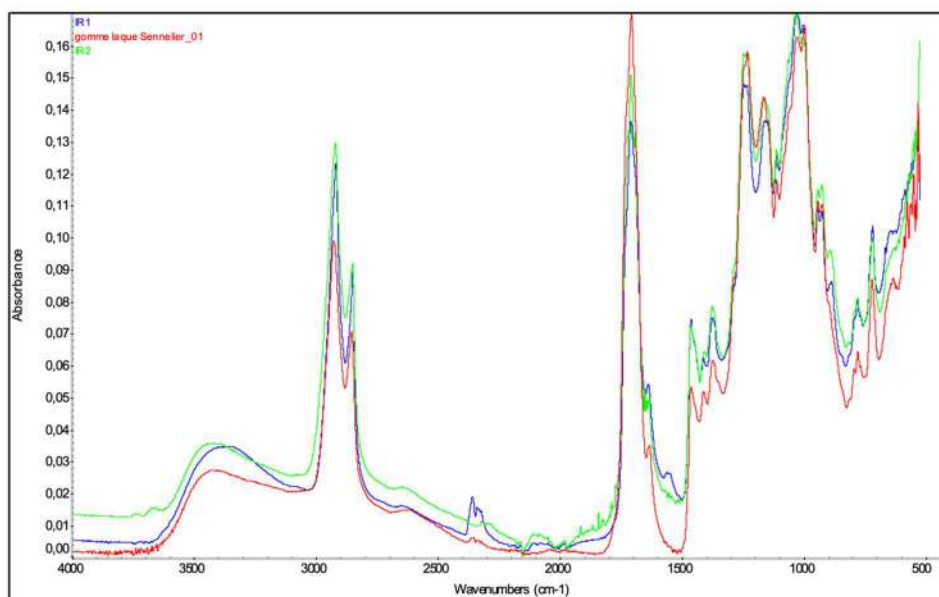


Figure 52. FTIR spectra in ATR mode of the varnish chip (IR1) in blue, the varnish chip (IR2) in green, and the shellac [®]Sennelier reference in red.

Radiocarbon results

The shellac varnish sample MGD150 (GifA21341) under the soundhole on the bass side of the baroque violin n° inv. 1993.1.1 provided the following range of dates: [1643 – 1684] (38.2%), [1736 – 1803] (52.8%) and [1936 – ...] (4.4%)(Table 19). The [1736 – 1803] interval is compatible with the dendrochronological study which concluded that the making period was most likely in the late 18th c. The shellac varnish sample MGD149 (GifA21274) under the soundhole on the treble side of the violin yielded a range of dates: [1528 – 1550] (8.7%), [1634 – 1665] (79.9%) and [1784 – 1794] (6.8%)(Table 19, Figure 53). The [1784 – 1794] interval is compatible with the dendrochronological study.

Table 19. ¹⁴C results on the MGD149 and MGD150 samples of the coating of the baroque violin, n°inv. 1993.1.1. The EA-GIS interface was used to produce and introduce the CO₂ into the ECHOmicADAS gas source. Calibration was done with IntCal20 (Reimer et al. 2020) thanks to the OxCal v4.4 software (Bronk Ramsey 2009).

sample ID				Description	Chemistry	Mass [µgC]	raw data		processed data	
N° inv.	MGD ID	Chemistry ID	measurement ID				F ¹⁴ C	±	Acomb/An	IntCal20 cal. ranges [AD] (95.4%)
1993.1.1	MGD149	GifA21274.1	ECHO-4577	varnish run under the soundhole (treble side)	A	989	0.9686	0.0025	141 /50.0	[1528 – 1550] (8.7%) [1634 – 1665] (79.9%) [1784 – 1794] (6.8%)
		GifA21274.2	ECHO-5012				0.9665	0.0048		
1993.1.1	MGD150	GifA21341.1	ECHO-4598	varnish run under the soundhole (bass side)	A	473	0.9741	0.0025	141.1/50.0	[1643 – 1684] (38.2%) [1736 – 1803] (52.8%) [1936 – ...] (4.4%)
		GifA21341.2	ECHO-5015				0.9702	0.0049		

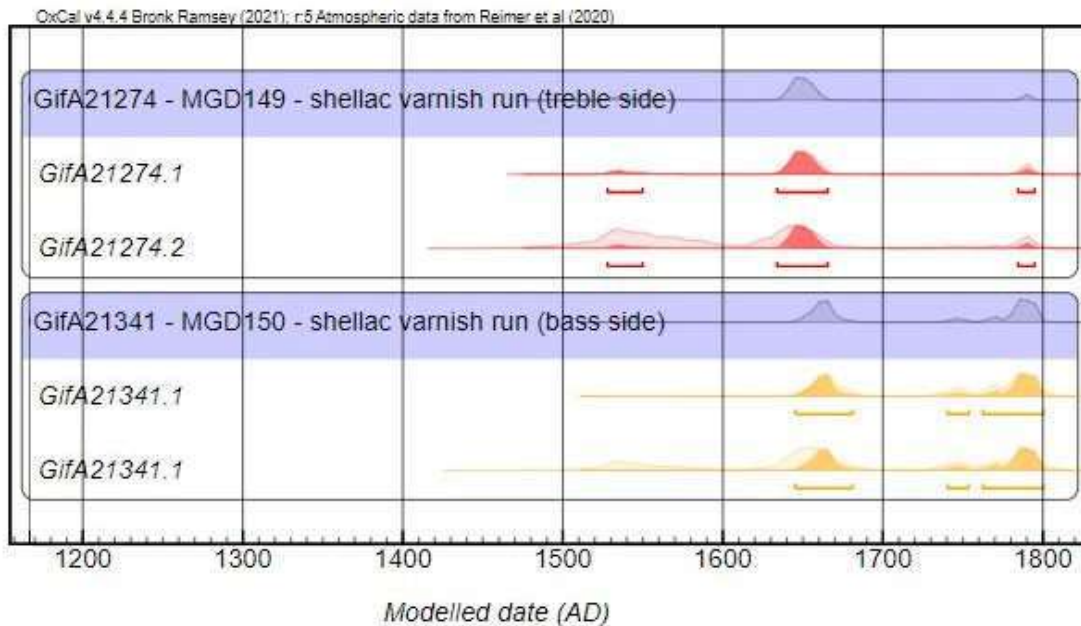


Figure 53. Calibrated range of dates using IntCal20 on the MGD149 and MGD150 samples of the coating of the baroque violin, n°inv. 1993.1.1

6.2.4. Violin, Vaillant, inv. 2015.8.1, coll. Musée de Mirecourt

Material history of the object

The violin, Vaillant, late 18th c. - early 19th c., Mirecourt, n° inv. 2015.8.1 (Figure 54) has an ink inscription on the back of the violin: “C.Vaillant”. Claude Joseph Vaillant was a violin maker from Mirecourt mentioned in registers from his wedding in 1778 until the French Revolution (Vannes, 1932). The stylistic dating is based on a specific violin making technique shared with the baroque violin, anonymous, c.1780, Mirecourt, n° inv. 1993.1.1. This violin is a rare testimony of the late 18th c. or the early 19th c.



Figure 54. Pictures of the violin, Vaillant, late 18th c. - early 19th c., Mirecourt, n° inv. 2015.8.1 (23.1x15.2x10.1cm) taken by Anne-Sophie Trivin © musée de Mirecourt. <http://www.musee-lutherie-mirecourt.fr/index.php?rub=collections&idmenu=2&limite=20>

Sampling location

A sample MGD151 for ^{14}C dating was taken near an area with a loss of varnish on the violin (Figure 54, Figure 55).



Figure 55. (from left to right) Pictures under visible light of the soundboard before and after the varnish sampling MGD151

6.2.5. Material characterization

The sample MGD151 was taken with a micro-scalpel under magnifying glass and UV light. The varnish layer is orange under UV light. Thus, a shellac varnish is more likely (Figure 56).

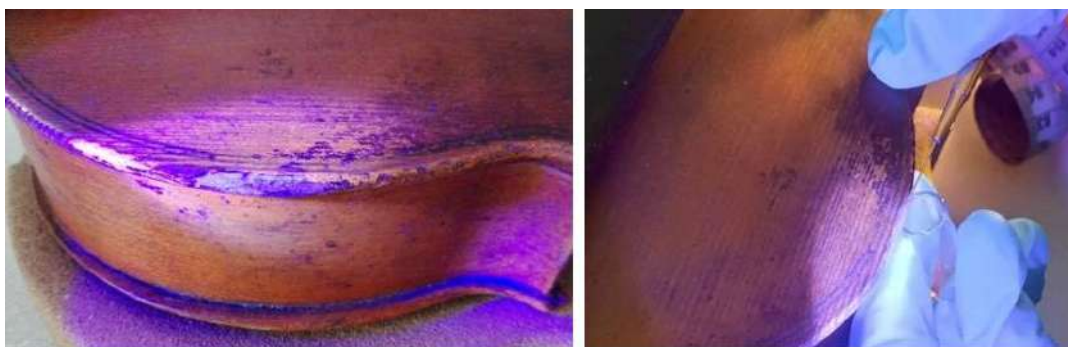


Figure 56. Pictures under UV light of the soundboard during the varnish sampling MGD151

6.2.6. Radiocarbon results

The shellac varnish sample MGD151 (GifA21342) on the violin n° inv. 2015.8.1 provided the range of dates: [1683 – 1735] (25.1%) and [1802 – 1930] (70.3%) (Table 20, Figure 57). The [1802 – 1930] interval is more compatible with the stylistic dating of the violin that was attributed to Vaillant, thus to the early 19th century. However, the soundboard has been highly exposed to maintenance interventions.

Table 20. ^{14}C results on the MGD151 sample of the coating of the violin, n° inv. 2015.8.1. The EA-GIS interface was used to produce and introduce the CO_2 into the ECHOMICADAS gas source. Calibration was done with IntCal20 (Reimer et al. 2020) thanks to the OxCal v4.4 software (Bronk Ramsey 2009).

sample ID				Description	Chemistry	Mass [μgC]	raw data				processed data
N° inv.	MGD ID	Chemistry ID	measurement ID				F^{14}C	\pm	year [BP]	\pm	IntCal20 cal. ranges [AD] (95.4%)
2015.8.1	MGD151	GifA21342	ECHO-4599	runner lower red coats	A	387	0.9855	0.0027	115	20	[1683 – 1735] (25.1%) [1802 – 1930] (70.3%)

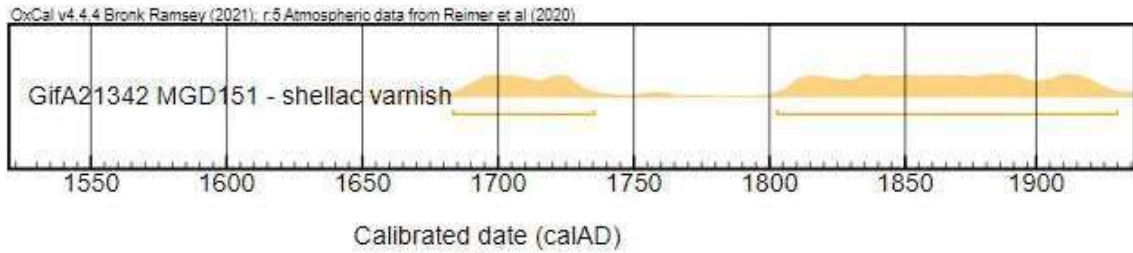


Figure 57. Calibrated range of dates using IntCal20 on the MGD151 sample of the coating of the violin, n°inv. 2015.8.1

6.3. Furniture with European and Asian lacquers

6.3.1. Cabinet André-Charles Boulle, inv. OA5468, coll. Louvre

Material history of the object

The cabinet with feet, OA5468, (which pairs with OA5469, Coll. Musée du Louvre, Département des Objets d'art du Moyen-Âge, de la Renaissance et des temps modernes) has a Boulle type marquetry with ebony, bamboo, wood, horn, ivory, copper and tin tortoise shell, brass decoration on a frame of oak, walnut and resinous wood. The central part is decorated with a figure of Louis XIV in Roman style clothes (Figure 58, left panel).

It is estimated that this cabinet was produced in the early years of André-Charles Boulle's activity in Paris (1685 – 1715?) during the reign of Louis XIV (1643-1715), as this kind of furniture went out of fashion after about 1700. The cabinet was modified at the request of Louis-Philippe around 1839. After being donated to the Louvre in 1870, the pair of cabinets was restored to its original version by the curator Emile Molinier and restored in 2015 (Alcouffe et al., 1993a).



Figure 58. a) Cabinet with feet OA5468 from a pair with OA5469 (dimensions: 1.870 x 0.990 x 0.510 m) manufactured by André-Charles Boulle, 1685-1715(?), Paris. © Musée du Louvre. <https://collections.louvre.fr/ark:/53355/cl010103617>, b) location of the sampling on the cabinet, c) sampling of lacquer chips in a glass tube with a 0.5 mm microchisel, d) observation of lacquer chips under binocular microscope.

Sampling location

The MGD123 sample was taken from behind the cabinet, on a cornice at mid-height, in order to be both discreet and in a location that had undergone as few restoration interventions as possible (Figure 58, right panel). After cleaning dust from the lacquered cornice with a precision wipe, the curator/restorer used a 0.5 mm microchisel (Electron Microscopy Sciences) to collect challenging thin lacquer chips in a glass tube (Figure 58, center panels).

Material characterization

The sample MGD123 was placed in an aluminium disposable and pre-baked weighing boat and observed under a binocular microscope (GifA20339). The lacquer chips are 10µm thick and have two layers: 1- a brown underlying layer applied on the wooden support, 2- a black top layer. This stratigraphy is typical of Martin's varnishes, imitating Asian lacquers (Chapter 1 – § 3.1).

Radiocarbon results

The range of dates obtained using ¹⁴C measurements was [1445 - 1657] (Figure 59, Table 21). This is much older than the expected age of the cabinet manufacture. This could be due to the effect of the underlying old wooden panel: if the lacquer sample included chips of wood, they would artificially age the ¹⁴C dating of the lacquer. We concluded that ¹⁴C dating confirms the practices of reuse of wooden panels during the making period estimated around 1700 according to stylistic comparison.

Table 21. ¹⁴C results on lacquer chips of the cornice at mid-height behind the cabinet OA5468. The CO₂ was produced on the micro-line and GIS cracking was used as interface to introduce the CO₂ into the ECHOmicADAS gas source. Calibration was done with IntCal20 (Reimer et al. 2020) thanks to the OxCal v4.4 software (Bronk Ramsey 2009).

sample ID				Chemistry	Mass [µgC]	raw data				processed data
N° inv.	MGD ID	Chemistry ID	measurement ID			F ¹⁴ C	±	year [BP]	±	IntCal20 cal. ranges [AD] (95.4%)
OA5468	MGD123	GifA20339	ECHO-3733	A	43	0.958	0.007	345	60	[1445 – 1657]

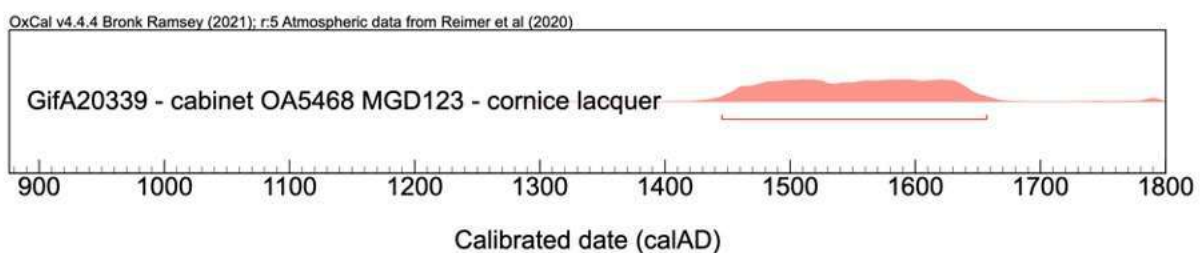


Figure 59. Calibrated range of dates using IntCal20 on lacquer chips of the cornice at mid-height behind the cabinet OA5468 (Reimer et al., 2020)

6.3.2. Chest of drawers Bernard II Van Risen Burgh, inv. OA11193, coll. Louvre

Material history of the object

The chest of drawers, OA11193, produced in Bernard II Van Risen Burgh's workshop (18th c., Paris, Coll. Musée du Louvre, Département des Objets d'art du Moyen-Age, de la Renaissance et des temps modernes) was delivered to Marie Leczinska in 1737 (Figure 60, right panel). This furniture then belonged to Madame Victoire during the reign of Louis XVI (Alcouffe et al.,

1993b, p.140). The central panel is a re-use of imported Japanese furniture with thick layers of lacquer, whereas the other panels are from lower quality Chinese panels with thinner lacquer layers. The joints between the Asian panels are filled with gilt bronze and a wood frame covered with even thinner layers of European lacquer, such as Martin's varnish. The Parisian *marchand-mercier* Thomas-Joachim Hébert is known to be one of the first to commission this kind of furniture, at least since 1720 (Forray-Carlier and Kopplin, 2014, p.72).

Sampling location

Two samples of lacquer were taken on the chest of drawers OA11193 (Figure 60):

- The sample MGD124 was taken from under a gilt bronze placed on a cabinet leg. Martin's varnish was too thin to be sampled; however, Chinese lacquer was collected and weighed as a powder in a glass tube (Figure 3a and Figure 4a).
- The sample MGD125 is a peeled fragment of thick Japanese lacquer with an underlying white glue. This sample was taken under a gilt bronze placed to hide a connection between the Japanese and the Chinese lacquered panels in the front of the chest of drawers (Figure 60b and Figure 61b).



Figure 60. a) Sampling of Chinese lacquer chips (MGD124), b) sampling of Japanese lacquer chips (MGD125) under gilded bronzes, c) chest of drawers, Bernard II Van Risen Burgh, c.1737, Paris, inv. OA11193, (dimensions: 84,3 x 127,5 x 61 cm). © Musée du Louvre. <https://collections.louvre.fr/ark:/53355/cl010104579>

Material characterization

The lacquer samples MGD124 and MGD125 were placed in an aluminum capsule and observed under a binocular microscope in order to identify the different layers and to mechanically separate them with microchisels for ^{14}C dating (Figure 61a).

The stratigraphy of the sample MGD124 (around 20 μm thick) is typical of Chinese lacquers and is thicker than those of Martin's varnishes (shellac and black pigments?) (see Cabinet Boulle OA5468 — § 6.3.1). The Chinese lacquer sample was divided into two sub-samples:

- Black chips of the upper layer (GifA20340.1)
- Brown chips of the lower layer (GifA20340.2)

The Japanese lacquer sample MGD125 is thicker than the Chinese lacquer with a similar stratigraphy that was divided into three sub-samples:

- White glue that stuck the chip of Japanese lacquer on the wood support (GifA20341.1)
- Brown chips of the lower layer (GifA20341.2) (Figure 61c)
- Black chips of the upper layer (GifA20341.3) (Figure 61d)



Figure 61. a) Chips of the MGD124 sample of Chinese lacquer with black and brown layers visible using a binocular microscope, b) the MGD125 sample of Japanese lacquer with an underlying white glue, c) mechanical abrasion of the brown lower layer of the Japanese lacquer sample MGD125, d) black upper layer of the Japanese sample MGD125.

Radiocarbon results

The black upper layer from Japanese lacquer (GifA20341.3) contained enough carbon to seal two gas tubes (GifA20341.3a and GifA20341.3b) and thus two measurements. The ^{14}C results of the two measurements were combined using the OxCal options: [1483 – 1661] (Table 22). The brown chips of Japanese lacquer (GifA20341.2) gave the intervals [1410 – 1530] and [1539 – 1635].

After ^{14}C measurements and calibration, the black chips of Chinese lacquer (GifA20340.1) provided the intervals [1402 – 1529] and [1542 – 1634]. The brown chips of Chinese lacquer (GifA20340.2) provided the intervals [1301 – 1370] and [1378 – 1456].

The sample of white glue was too small to give a reliable result.

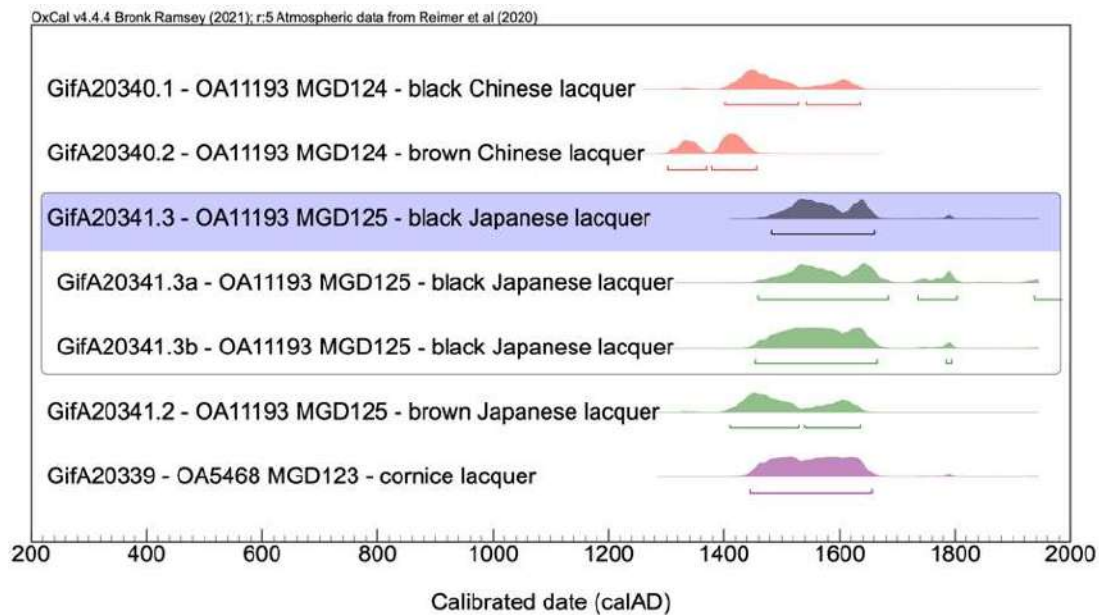


Figure 62. Calibrated range of dates using IntCal20 on Chinese lacquer sample MGD124 and the Japanese lacquer sample MGD125 behind gilded bronzes on the front of the chest of drawers OA11193 (Reimer et al., 2020)

^{14}C measurements on brown and black Japanese lacquers from the chest of drawers OA11193 are in a good agreement with an Acomb of 71.1 for a threshold of 50.0. This yields a single interval of time, [1475 – 1640], covering unfortunately, the whole of the 16th century.

Likewise, the brown and black layers of the Chinese lacquer are in good agreement (Acomb = 108.4%), giving a time range mostly located in the first half of the 15th c., [1328 – 1346] (2.5%) and [1395 – 1475] (93.0%).

While the ^{14}C investigation did not prove very relevant to provide a precise age of the object, it clearly confirms the seniority of the Chinese and Japanese lacquers whose ages are much older than the production year in the workshop of Bernard II Van Risen Burgh, for a delivery in 1737, showing that Asian lacquered panels were reused to satisfy the European appetite for the imitation of Asian lacquers.

In detail, the ^{14}C ages obtained on the Chinese lacquer seem to indicate an older age for the lower layer (brown) than for the upper layer (black)(Figure 62). This tendency could be a reminiscent of an underlying old wooden support (Durier et al., 2021). The removal of the lower layer could have included chips of wood from the reused lacquered panels and thus artificially aged the ^{14}C dating of the lower lacquer layer. Then, we combined the Japanese lacquer layers and the black layer of the Chinese lacquer. This resulted in an Acomb of 58.6, slightly higher than the threshold of 50.0 and for the [1456 – 1529] and [1544– 1634] intervals.

6.4. Horse-drawn carriages and sleds

The sleds from the collections of the château de Compiègne, Musée National de la Voiture et du Tourisme (MNVT) and the Royal Museums for Art and History, Brussels, Belgium (KMKG-MRAH) are in a fair state of conservation as they were used only once or twice a year in the past by their noble owners due to the temperate environment of their locality (Forray-Carlier and Kopplin, 2014, p.210). Little is known about those collections, and, more broadly, little is known about the techniques and materials used to coat pre-industrial sleighs, sleds and carriages.

The sled collection of the château de Compiègne is a donation from the Société des amis du Musée collected in the 1930s when the use of horse-drawn vehicles became completely obsolete. The documentation has been lost due to bombardment during World War II. During this PhD, the composition of the varnish layers was identified based on the knowledge of traditional techniques and observations by the restorer ([Chapter 1 – § 3.3](#)).

In the same way, little documentation subsists on the TR1868, TR88, TR41 sleds of the collection of the Royal Museums for Art and History (RMAH). The original coats were preserved and were occasionally covered with some overpainting. The composition of varnish stratigraphies was identified in the framework of the Elinc project (2012-2018) based on material characterization analyses.

See [Appendix 3 – § 2](#) for more details on the sampling at Compiègne and Brussels.

6.4.1. Snake and shell sled, inv. CMV66, coll. MNVT

Material history of the object

The snake and shell sled is assumed to have been manufactured in the early 18th c. It was acquired at a public auction at the Hôtel Drouot in Paris on 10th February 1936 from the family of the architect Mewes, Alsace.

The sled underwent restoration interventions over time such as undated repainting on cracks and joints with gouache and water-based paint. Several parts of worm-eaten wood have been treated with xylamon (Cyfluthrin $C_{22}H_{18}Cl_2FNO_3$, Azaconazol $C_{12}H_{11}Cl_2N_3O_2$) and it is likely that a boiled-oil surface layer was also applied in 1962 by brigadier Piéri, keeper Mangin and Lesueur, as they did for several other carriages of the museum collection. Restoration was carried out in 1996 to re-glue varnish chips using an acrylic binder (Plextol B 500 B 360 2:3, 1/3 at 50% in water).

Sampling location

The coating stratigraphy on the shell-shaped body is believed to be original according to the restorer's expertise and it comprises:

- 1- a white preparation layer with carbonates (lead white or chalk)
- 2- a varnish surface with brown, red and yellow earth pigments.

The restorer sampled the marbled yellow coating (CMV66-1), as well as the marbled brown coating (CMV66-2), on the left side of the shell-shaped body separately from the preparation layer using a chisel with a new blade (Figure 63).

A sample was also taken separately from the white preparation layer on the front side of the gilded dashboard near a carved eagle (CMV66-3) (Figure 63). This stratigraphy comprises:

- 1- oil gilding using traditional technique (18th c. or 19th c.) applied on a white preparation layer (lead white or chalk)
- 2- a dark surface layer (19th c.) which is a later decoration using bronze overpaint, also called bonzine by restorers (copper powder with varnish).

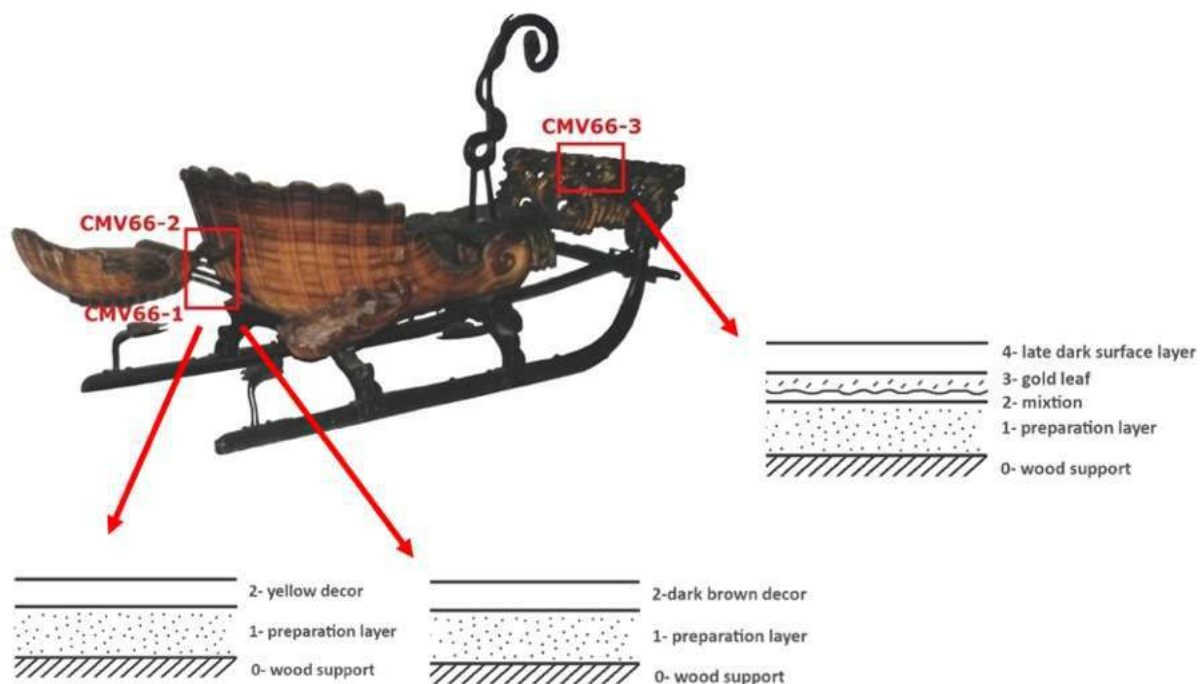


Figure 63. Location of the samples CMV66-1, -2 and -3 with their simplified stratigraphy on the snake and shell sled (inv.CMV66, © MNVT, Compiègne) (long.275 x large 110 x high 155 cm).

Material characterization

The marbled yellow sample MGD134 on the shell-shaped body (CMV66-1) was observed using a binocular microscope to verify the absence of contamination by the preparation layer during the sampling (Figure 64). The composition of this sample is estimated to be a traditional mixture of yellow ochre pigments with an oil-based binder.

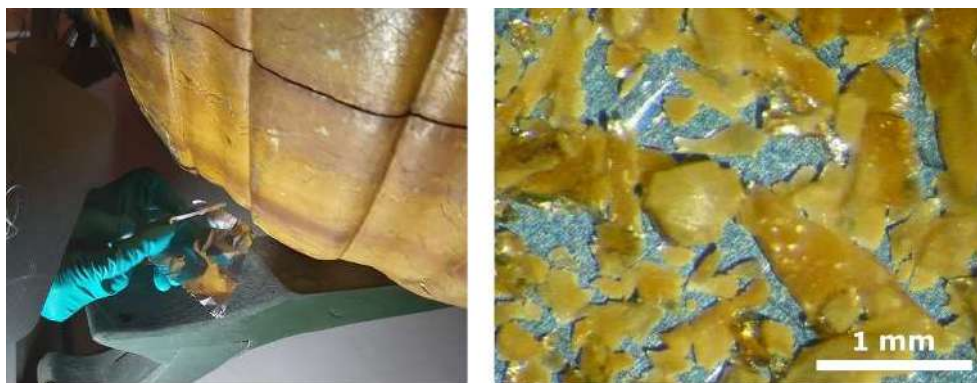


Figure 64. (left) The marbled yellow coating MGD134 on the left side of the shell-shaped body of the snake and shell sled (CMV66-1), (right) picture of the sample under binocular microscope (GifA20350)

The marbled brown sample MGD135 on the shell-shaped body (CMV66-2) was observed using a binocular microscope to verify the absence of contamination by the preparation layer during the sampling (Figure 65). The composition of this sample is estimated to be a traditional mixture of earth pigments with an oil-based binder.

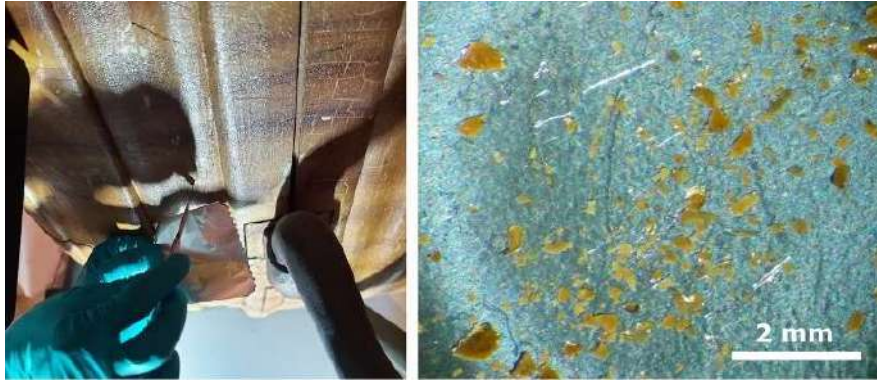


Figure 65. (left) The marbled brown coating MGD135 on the left side of the shell-shaped body of the snake and shell sled (CMV66-2), (right) picture of the sample under binocular microscope (GifA20351)

The gilded layer sample MGD136 on the dashboard of the sled (CMV66-2) was observed using a binocular microscope to verify the absence of contamination by the preparation layer during the sampling (Figure 66). The composition of this sample is relevant with a traditional oil gilding comprising an oil/resin mixtion under a gold leaf (c.18th c.). It was covered by a thin organic varnish with a bronze patina (c.19th c.). Mechanical separation of the original gilded layer and the bronzine layer was performed using micro-chisels under binocular microscope (GifA20352, Figure 66):

- Original oil/resin varnish c.18th c. (GifA20352.1)
- Remains of darker chips from the upper varnish c.19th c. (GifA20352.2)



Figure 66. (left) The gilding layer sample MGD136 on the front side of the gilded dashboard near a carved eagle on the snake and shell sled (CMV66-3), (right) picture of the sample under binocular microscope (GifA20352)

Radiocarbon results

The collected samples were subjected to the following treatment steps: 1- sampling (August 2020), 2- decontamination by chemistry using mainly the A protocol (§ 4.1.2) (September 2020), 3- micro-line and cracking-GIS, 4- physical measurements, and lastly 5- validation of ¹⁴C results including Bayesian statistics (May 2021⁵⁰). The combustion of the yellow varnish (MGD134, GifA20350) and of mixtion (MGD36.1, GifA20352.1) provided enough CO₂ to be split and sealed in two micro-tubes in order to duplicate the measurement. The results of individual measurements and their combinations are shown in Table 23.

⁵⁰ The dates August-September 2020 and May 2021 are only indicated here to consider the time needed to perform the ¹⁴C dating protocol during the pandemic Covid-19.

Table 23. ¹⁴C results on the marbled yellow and brown samples (MGD124, MGD135) and the gilded sample (MGD136) on the snake and shell sled inv. CMV66. The CO₂ was produced on the micro-line and GIS cracking was used as an interface to introduce the CO₂ into the ECHOMICADAS gas source. Calibration was done using IntCal20 (Reimer et al. 2020) thanks to the OxCal v4.4 software (Bronk Ramsey 2009).

sample ID					Chemistry	Mass [µgC]	raw data				processed data			
N° inv.	MGD ID	Chemistry ID	measurement ID	Description			F ¹⁴ C	±	year [BP]	±	Acomb /An	IntCal20 cal. ranges [AD] (95.4%)	Acomb /An	IntCal20 cal. ranges [AD] (95.4%)
CMV66-1	MGD134	GifA20350a	ECHo-3950.1	yellow varnish	A	47	0.949	0.007	420	60	118.7 / 50.0	[1429 – 1524] (69.2) [1559-1631] (26.3)	111.4 / 50.0	[1439 – 1524] (69.0) [1571 – 1630] (26.4)
		GifA20350b	ECHo-3950.2			63	0.952	0.007	390	60				
CMV66-2	MGD135	GifA20351	ECHo-3951	brown varnish	A	93	0.955	0.007	370	50	-	[1442 – 1639] (95.4)		
CMV66-3	MGD136.1	GifA20352.1a	ECHo-3951.1.2	mixture	A	54	0.975	0.007	200	60	126.1 / 50.0	[1639 – 1698] (26.1) [1722 – 1814] (48.8) [1835 – 1884] (6.0) [1910 - ...] (14.6)	107.2 / 50.0	[1642 – 1698] (24.1) [1722 – 1814] (49.8) [1836 – 1882] (6.2) [1910 - ...] (15.4)
		GifA20352.1b	ECHo-3952.1.1			68	0.975	0.007	200	60				
	MGD136.2	GifA20352.2	ECHo-3953.1.1	bronzine	A	12	0.982	0.014	150	110	-	[1515 – 1590] (7.2) [1620 - ...] (88.2)		

Analysis of the results clearly shows that MGD134 and MGD135, from the body of the sled, are contemporaneous. The combination of the ^{14}C results produces good agreement ($A_{\text{comb}} = 111.3\%$) and yields the intervals [1439–1524] (69.0%) and [1571–1630] (26.4%) (Table 23, Figure 67).

The carbon content of 12 μgC in the bronzine sample MGD36.2 (GifA20352.2) was not enough to provide narrow intervals of dates: [1515–1590] (7.2%) and [1620 - ...] (88.2%). However, this result could be combined with the ^{14}C measurement on the oil mixtion MGD36.1 (GifA20352.1) of the dashboard of the sled (CMV66-2): [1642 –1698] (24.1%), [1722 –1814] (49.8%), [1836 –1882] (6.2%), [1910 – ...] (15.4%) (Table 23, Figure 67).

^{14}C measurements confirmed that the coating of the shell body is dated prior to the coating of the gilded dashboard and runners. ^{14}C dating also revealed that the initially expected “protective” coat made of linseed oil from the 1960s was not applied. However, the ^{14}C results on the body of the sled give older ages than the expected period of the early 18th c., which means that the application of a restoration/maintenance product must have aged the original marbled coat (such as xylamon or acrylic).

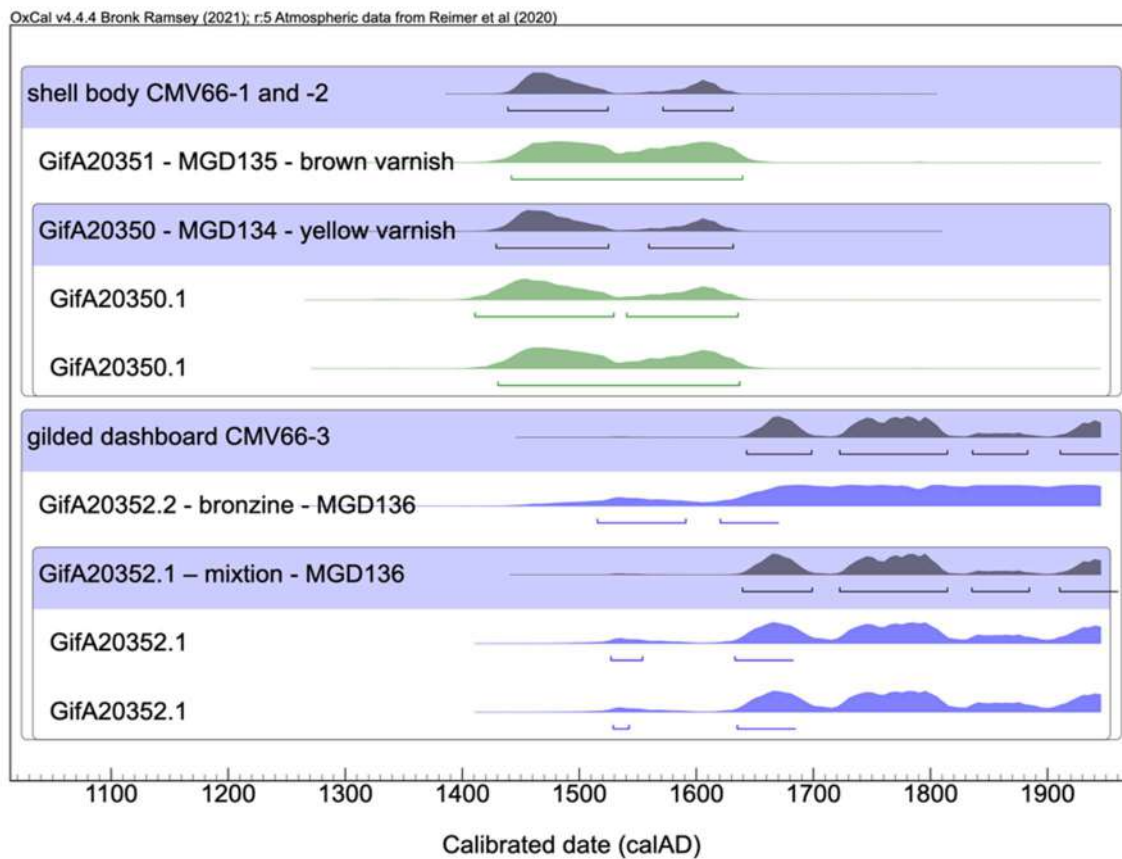


Figure 67. Calibrated range of dates using IntCal20 on the yellow sample MGD134 and the brown sample MGD135 on the body and the gilded sample MGD136 on the dashboard of the sled CMV66

6.4.2. Eagle sled, inv. CMV57.006, coll. MNVT

Material history of the object

The sled is a donation from the Vicomte de Chézelles in 1957. The undergear is estimated to be from the late 18th c. whereas the body is assumed to be original, i.e. from the 17th c. The left side of the sleigh is particularly worm-eaten. A xylamon treatment was applied against

insects and a boiled-oil surface layer was applied to the varnish coatings in 1961. In 1996 and 2009, restoration was carried out to re-glue varnish chips (acrylic resin Paraloid B 72 10%, ethyl acetate) on the body of the sleigh, the eagle and the runners.

Sampling location

The stratigraphy of sample CMV57.006-1 from the body of the eagle sled (17th c.) comprises: 1- a white preparation layer with carbonates (lead white or chalk), 2- an oil/resin mixtion, 3- gold leaf (17th c.), 4- thick dark layers with green pigments (copper acetate?) and bronzite, 5- linseed oil from the 1960s.

The stratigraphy of sample CMV57.006-2 (without the preparation layer) from the runners (18th c.) comprises: 1- a green layer (copper acetate?), 2- an upper dark layer. This sample was taken on the right runner at the junction with the front brace.

Lastly, the samples CMV57.006-3 and -4 were taken on the cloud-shape decoration of the body which has a coating stratigraphy comprising: 1-a pale blue preparation layer, 2- a varnish layer dated from 1961 (Figure 68).

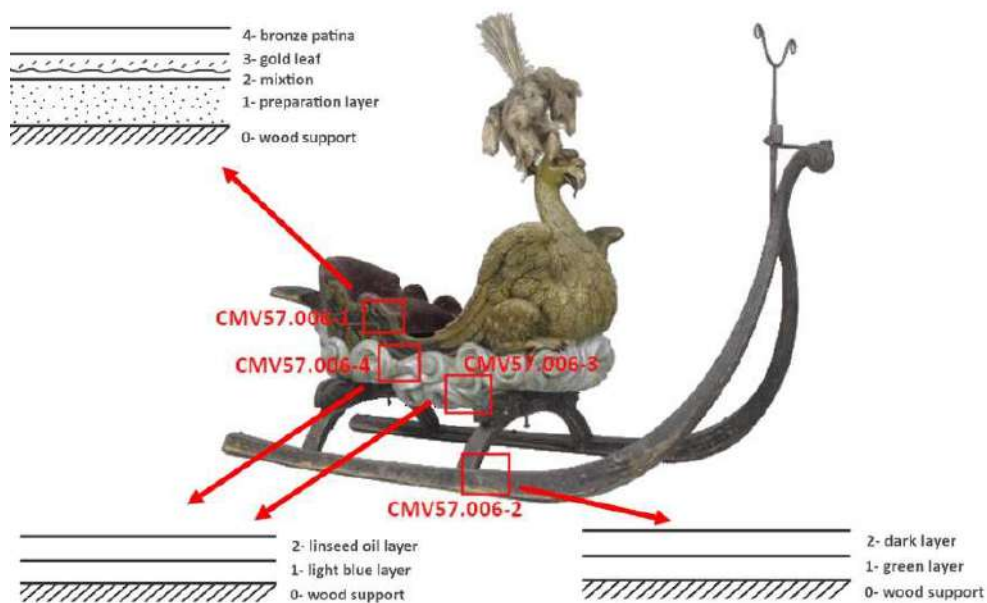


Figure 68. Location of the samples CMV57.006.1, -2, -3 and -4 with their simplified stratigraphy on the eagle sled (inv.CMV57.006, © MNVT, Compiègne) (long.295 x large 210 x high 95 cm).

Material characterization

The green and gilded sample MGD130 from the eagle body (CMV57.006-1) was observed under binocular microscope (Figure 69). The surface was slightly scattered using a microchisel to remove a possible upper varnish applied in the 1960s. The lower green layer was analysed using ¹⁴C dating (GifA20346).



Figure 69. (left) The green and gilded sample MGD130 taken without the preparation layer on the right side of the body of the eagle sled (CMV57.006-1), (right) picture of the sample under binocular microscope (GifA20346)

The green sample MGD131 from the right runner (CMV57.006-2) was taken as a bulk due to its friability (GifA20347).

The pale blue sample MGD132 from the cloud-shaped body (CMV57.006-3) was separated from the upper oil layer applied in the 1960s. Under binocular microscope, the sample was found to comprise brown chips and green-blue layers (GifA20348).

The sample MGD133 from the cloud-shaped body (CMV57.006-4) only comprises boiled oil dated from an intervention in the 1960s (Figure 70).



Figure 70. (from left to right) green sample MGD131 from the right runner (CMV57.006-2), the pale blue sample MGD132 under the cloud body (CMV57.006-3), sample MGD133 of the boiled oil applied in the 1960s, taken from the cloud body (CMV57.006-4)

Radiocarbon results

The collected samples were subjected to the following treatment steps: 1- sampling (August 2020), 2- decontamination by chemistry using essentially the A protocol (§ 4.1.2) (September 2020), 3- micro-line and cracking-GIS, except for MGD133 which was transformed using EA-GIS, 4- physical measurements, and lastly 5- validation of ^{14}C results including Bayesian statistics (from December 2020 to February 2021).

Surprisingly, the varnish supposedly dated from the 1960s yielded the range of dates: [705-737] (3.2%), [771-1026] (92.2%). An assumption is that a petroleum-based varnish was applied evenly on the sled and might be mainly responsible for the apparent ageing of the coats.

By combining the ^{14}C results on the green coat, the MGD131 sample provided the following range of dates: [1295-1410] (95.4%). These results are similar to the range of dates provided by the pale blue sample MGD132: [1406-1445] (95.4%)(Table 24). However, these ^{14}C measurements are not in agreement with the dating of the sled by stylistic comparison (Figure

71). Moreover, ^{14}C results do not show that the coating of the body is dated prior to the coating of the undergear as initially expected.

Consequently, an explanation for the ageing of the green and pale blue coats is that the restoration interventions on the sled (which has been heavily retouched) affected the ^{14}C measurements, namely:

- i- bronzine layer applied on the green coats containing a varnish with carbon that post-dates the 19th c.
- ii- xylamon applied especially on the left side (including the runners) containing dead carbons ($F^{14}\text{C}=0$),
- iii- chips of varnish globally re-glued and partly repainted with acrylic derivatives ($F^{14}\text{C}=0$)
- iv- petroleum-based varnish evenly applied on the sled in the 1960s.

The chips of varnish are brittle and the underlying preparation coats (more absorbent than the upper layers) were more easily accessible, facilitating the incorporation of restoration products.

Table 24. ^{14}C results on the MGD130, MGD131, MGD132 and MGD133 samples of the coating layers of the eagle sled CMV57.006. The CO_2 was produced on the micro-line and cracking GIS was used as an interface to introduce the CO_2 into the ECHO MICADAS gas source. Calibration was done using IntCal20 (Reimer et al. 2020) thanks to the OxCal v4.4 software (Bronk Ramsey 2009).

sample ID				Description	Chemistry	Mass [μgC]	raw data				Acomb / An	processed data
N° inv.	MGD ID	Chemistry ID	measurement ID				F^{14}C	\pm	year [BP]	\pm		
CMV57.006-1	MGD130.2	GifA20346	no gas	green and gilded coats	A							
CMV57.006-2	MGD131	GifA20347a	ECHo-3739.1.1	green coats	A	170	0.9268	0.0065	610	55	110.5 / 50.0	[1295 – 1410] (95.4%)
		GifA20347b	ECHo-3739.1.2			127	0.9278	0.0063	600	55		
CMV57.006-3	MGD132	GifA20348	ECHo-3744	pale blue coat	A	425	0.9396	0.0026	500	20	-	[1406 – 1444] (95.4%)
CMV57.006-4	MGD133	GifA20349	ECHo-3815	boiled oil	A	83	0.8680	0.0072	1 135	65	-	[705 – 737] (3.2%) [771 – 1026] (92.2%)

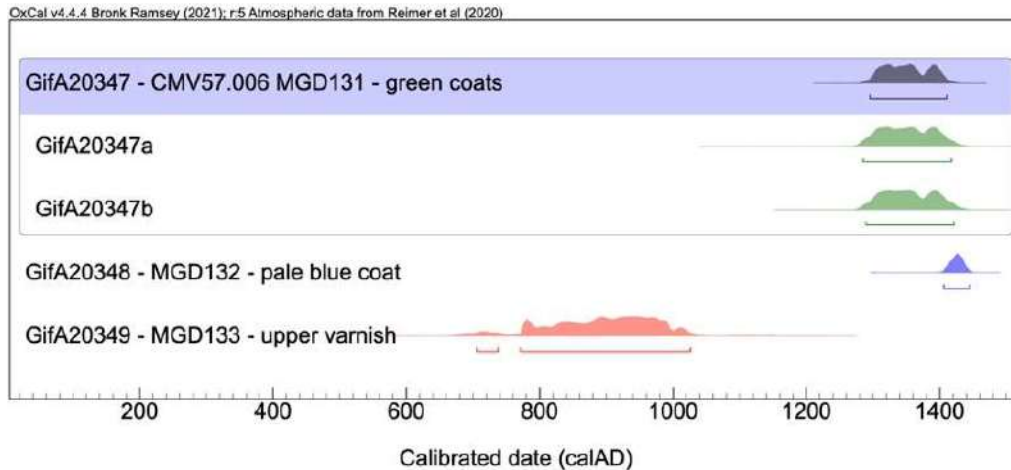


Figure 71. Calibrated range of dates using IntCal20 on the MGD130, MGD131, MGD132 and MGD133 samples of the coating layers of the eagle sled CMV57.006 (Reimer et al., 2020).

6.4.3. Dragon sled, inv. CMV64, coll. MNVT

Material history of the object

The dragon sled CMV64 was given to the museum in 1927 with little information on its origin. The body is assumed to date from the 18th c. However, the undergear might date from the second half of the 19th c. due to its typical coil spring suspensions. The sled was still in use during the 2nd Empire at the time of Empress Eugénie. The coats from the 19th c. were removed before the application of a boiled oil "protective" layer in the 1960s. As for the eagle sled, the coating is very cracked, brittle and sensitive to any perturbation and was heavily retouched. Chips of varnish were re-glued with beeswax and dammar resin (80/20) during a restoration in 1996.

Sampling location (Figure 72)

The samples CMV64-1 and CMV64-2 (Figure 72) were taken on the left runner under a coil spring suspension estimated to date from the 19th c. According to the restorer, the complete stratigraphy on the runners comprises:

- 1- a light pink preparation layer with carbonates (lead white or chalk)
- 2- dark red lacquer with vermilion
- 3- a thick brown-red layer
- 4- a thin brown oil/resin mixtion
- 5- gold leaf.

On the left back of the dragon body, the sample CMV64-3 was taken on the end of an acanthus leaf with a stratigraphy of:

- 1- preparation layer
- 2- resin/oil mixtion
- 3- gold leaf
- 4- yellow coat.

The sample CMV64-4 was taken without the preparation layer on a silvery grey scale with the following stratigraphy: 2-oil/resin mixtion, 3-silver leaf, 4-darker upper layer.

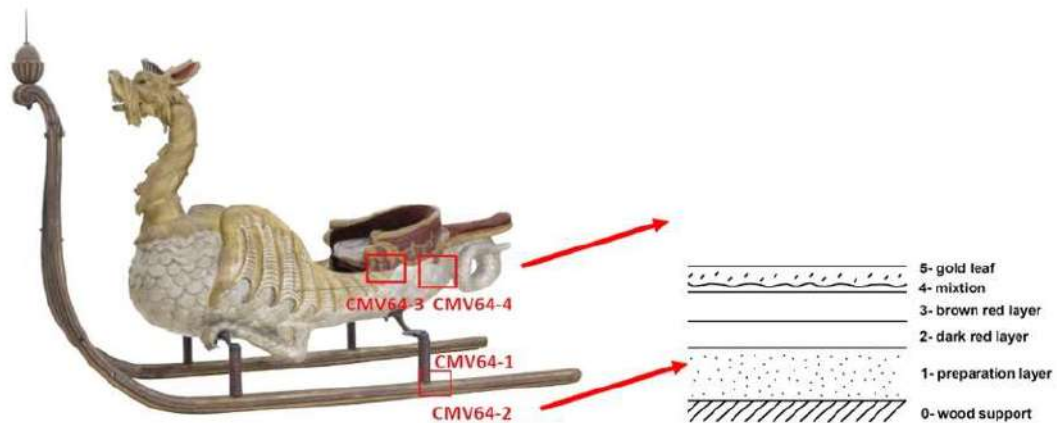


Figure 72. Location of the samples CMV64-1, -2, -3 and -4 on the dragon sled (inv. CMV64, © MNVT, Compiègne) (long.245 x large 100 x high 175 cm).

Material characterization

The red and gilded sample MGD126, taken without the pink preparation layer, from the left runner of the dragon sled (CMV64-1) was observed under binocular microscope and showed a more complex stratigraphy than under a visual examination. The MGD126 sample was divided into 3 sub-samples under binocular microscope (Figure 73):

- Upper layer with oil/resin mixtion and gold leaf (GifA20342.1)
- Middle red-brown coat (GifA20342.2)
- Lower red coat (GifA20342.3)



Figure 73. (left) The red and gilded sample MGD126 taken without the preparation layer on the left runner of the dragon sled (CMV64-1), (right) picture of the sample under binocular microscope (GifA20342)

The red and pink sample MGD127 from the left runner of the dragon sled (CMV64-2) was observed under binocular microscope (GifA20343) (Figure 74). The sample includes: 1- a pink preparation layer, 2-red lacquer. It might contain a red pigment (vermillion), turpentine, an oil binder and lead white or chalk.



Figure 74. (left) The sample MGD127 with the dark red and the pink preparation layers taken on the left runner of the dragon sled (CMV64-1), (right) picture of the sample under binocular microscope (GifA20343).

The sample MGD128 from the golden acanthus leaf of the dragon body (CMV64-3) was observed and divided into sub-samples under binocular microscope (GifA20344) (Figure 75):

- Resin/oil mixtion with gold (GifA20344. 1)
- Remains of the sample (yellowish coat) (GifA20344. 2)



Figure 75. (left) The golden sample MGD128 taken on the left back side of the body of the dragon sled (CMV64-3), (right) picture of the sample under binocular microscope (GifA20344).

The sample MGD129 from the grey scale of the dragon body (CMV64-4) was observed under binocular microscope (GifA20345). It is exempt of the preparation layer and comprises: 2-an oil mixtion, 3-silver leaf, 4-a darker upper layer (Figure 76).



Figure 76. (left) The grey sample MGD129 taken on the left back side of the body of the dragon sled (CMV64-4), (right) picture of the sample under binocular microscope (GifA20345)

Table 25. ^{14}C results on the MGD126, MGD127, MGD128 and MGD129 samples of the coating of the dragon sled CMV64. The CO_2 was produced on the micro-line and the cracking-GIS was used as interface to introduce the CO_2 into the ECHOMICADAS gas source. Calibration was done using IntCal20 (Reimer et al. 2020) thanks to the OxCal v4.4 software (Bronk Ramsey 2009).

sample ID				Description	Chemistry	Mass [μgC]	raw data				processed data	
N° inv.	MGD ID	Chemistry ID	measurement ID				F^{14}C	\pm	year [BP]	\pm	Acomb / An	IntCal20 cal. ranges [AD] (95% proba)
CMV64-1	MGD126	GifA20342a	ECHo-3736.1.1	gilded coat	A	137	0.926	0.006	615	55	104.4 / 40.8	[1293 – 1400] (95.4%)
		GifA20342b	ECHo-3736.1.2	brown-red coats	A	96	0.920	0.007	670	60		
		GifA20342c	ECHo-3736.1.3	red coats	A	76	0.929	0.007	590	60		
CMV64-2	MGD127	GifA20343	ECHo-3737	pink preparation coat	A	48	0.944	0.008	470	70	-	[1316 – 1360] (8.4%) [1388 – 1528] (72.5%) [1552 – 1634] (14.5%)
CMV64-3	MGD128	GifA20344.1	ECHo-3732.1.1	gilded coat	Thermolysis ($T < 400^\circ\text{C}$)	88	0.489	0.004	5 750	75	-	
			no gas		Thermolysis ($400-850^\circ\text{C}$)							
		GifA20344.2	no gas	yellowish coat	Thermolysis ($T < 400^\circ\text{C}$)							
			ECHo-3732.2.1		Thermolysis ($400-850^\circ\text{C}$)	88	0.491	0.004	5 715	65	-	
CMV64-4	MGD129	GifA20345	ECHo-3743	silver coat	A	948	0.905	0.003	805	20	-	[1216 – 1272] (95.4%)

Radiocarbon results (Table 25, Figure 77)

For all the layers in the sample MGD126 of the sled left runner (CMV64-1), the ^{14}C contents are statistically similar and the high Acomb of 104.4% (threshold at 40.8%) acknowledged their combination, that provides the range of dates: [1296 - 1400] (95.4%), i.e. much older than the age of the sled. Despite the difference in composition of the different layers, the coats have a highly reproducible ^{14}C contamination (Figure 77). It is highly probable that restoration products were (at least partly) petroleum derivatives ($F^{14}\text{C}=0$) and that they contaminated the layers on which they were applied by diffusion. However, the underlying preparation layer (GifA20343) from the same varnish stratigraphy (MGD127) yielded younger ranges of dates: [1316 - 1361] (8.4%), [1388 - 1528] (72.5%), [1553 - 634] (14.5%). This layer seems to have been less contaminated than the upper layers, but the dating is also too old.

The silver sample MGD129 (GifA20345) on the body of the sled (CMV64-4) provides an older range of dates: [1216 - 1272] (95.4%). This sample was analysed as a bulk with the original gilding and an upper restoration layer applied in the 1960s. The resulting ^{14}C age is within the order of the ^{14}C age of the left runner and once again, the dating is older than expected. Here also, the most likely hypothesis is contamination by restoration products containing petroleum derivatives.

The sample MGD128 was mechanically divided into two parts: the lower gilded part and the yellowish surface layer. Each sub-sample was thermally decomposed according to two temperature steps: [0-400°C] and [400-800°C]. This was done in an attempt to get rid of the carbons that could come from the preparation layer, presumably lead white. According to Beck et al. (2019) the [0-400°C] fraction should contain carbons contemporaneous with the manufacture of the lead white and hopefully, no geological carbon residue from the lead white ingredients. The high temperature fraction of the gilded part and the low temperature fraction of the yellowish layer did not provide enough gas to be measured. The remaining part, treated respectively by thermolysis at $T < 400^\circ\text{C}$ and $T > 400^\circ\text{C}$, provided the following $F^{14}\text{C}$ results: 750 ± 75 BP and $5\ 715 \pm 65$ BP. It clearly indicates that i- the making of lead white left a significant amount of geological carbon in the final product, ii- the geological carbons were present in both temperature fractions, iii- the threshold of 400°C was likely not the appropriate one. Indeed, Messager et al. (2020) subsequently showed that 300°C was a better threshold than 400°C. We therefore lost the opportunity to date the lead white we were expecting in the low temperature fraction. Furthermore, this attempt also showed that thermal decomposition to extract the organic part of a lead white/chalk mixture is not the best protocol to use. A choice should be made: either dating the lead white manufacture with thermal decomposition below 300°C or dating the organic fraction after sample leaching using acid treatment before combustion. It is not possible to obtain both results from the same subsample.

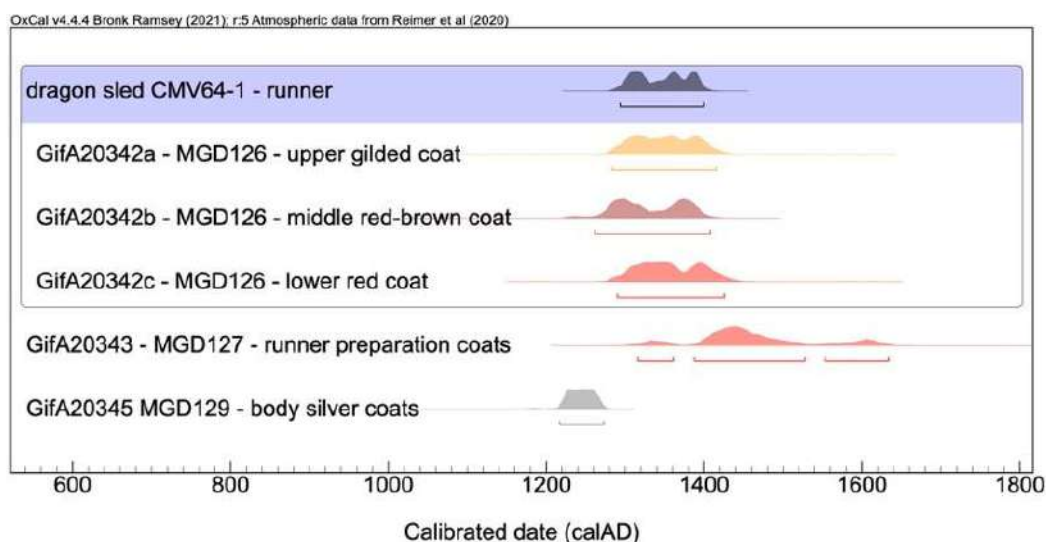


Figure 77. Calibrated range of dates using IntCal20 on the MGD126, MGD127, MGD128 and MGD129 samples of the coating layers of the dragon sled CMV64 (Reimer et al., 2020)

6.4.4. The golden Berlin carriage, inv. CMV64.002, coll. MNVT

Material history of the object

The golden Berlin carriage belonged to the Domergue family from the Agen region (Hôtel Agenois du Duc de Guillon, France). The previous owner claimed that this carriage was sold at an auction of Mme de Pompadour's property. Only the golden body remained after a fire. It was initially dated from 1760. However, stylistic comparisons indicate that it might have been manufactured during the first half of the 18th century (1730 – 1740?). The wormed wooden parts were treated with xylamon in 1964.

Sampling location

The CMV64.002-1 and CMV64.002-2 samples were taken from the bottom of a central door. Preparation layers are numerous and thick unlike the décor layer (Figure 78).

- 1- preparation layers (lead white or chalk)
- 2- dark layer
- 3- metallic leaf with an unknown ratio of gold and silver
- 4- silver leaf
- 5- reddish lacquer (shellac?)

To summarize, the stratigraphy comprises two successive gilded decors, several varnish layers with heterogeneous thicknesses, the last of which might be a restoration.



Figure 78. Location of the samples CMV64.002-1 and -2 on the golden Berlin carriage (inv. CMV64.002, © MNVT, Compiègne) (long.198 x large 120 x high 190 cm).

Material characterization

The sample MGD137 was taken without the preparation layers on the side of the central door (CMV64.002-1) and was observed under binocular microscope showing the thickness of the varnish layers (GifA20353) (Figure 79).

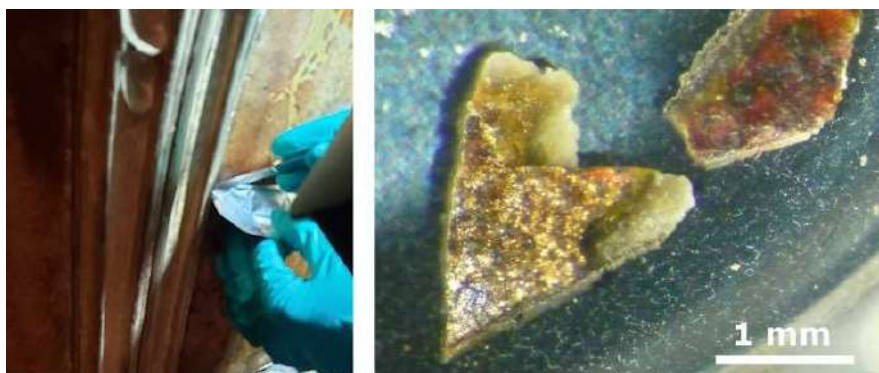


Figure 79. (left) The golden sample MGD137 taken on the left bottom side of a central door of the golden Berlin carriage (CMV64.001-1), (right) picture of the sample under binocular microscope (GifA20353)

The sample MGD138 was taken on the bottom corner of the central door of the Berlin carriage (CMV64.002-2). It is made of pigments, oil binder, shellac and metal leaves. The sample was divided into sub-samples and slight fibers of the wood support were removed under binocular microscope (Figure 80):

- The upper varnish with shellac (GifA20354.1)
- The hard white central coats (GifA20354.2)
- The soft preparation layer directly applied on the wood support (GifA20354.3)

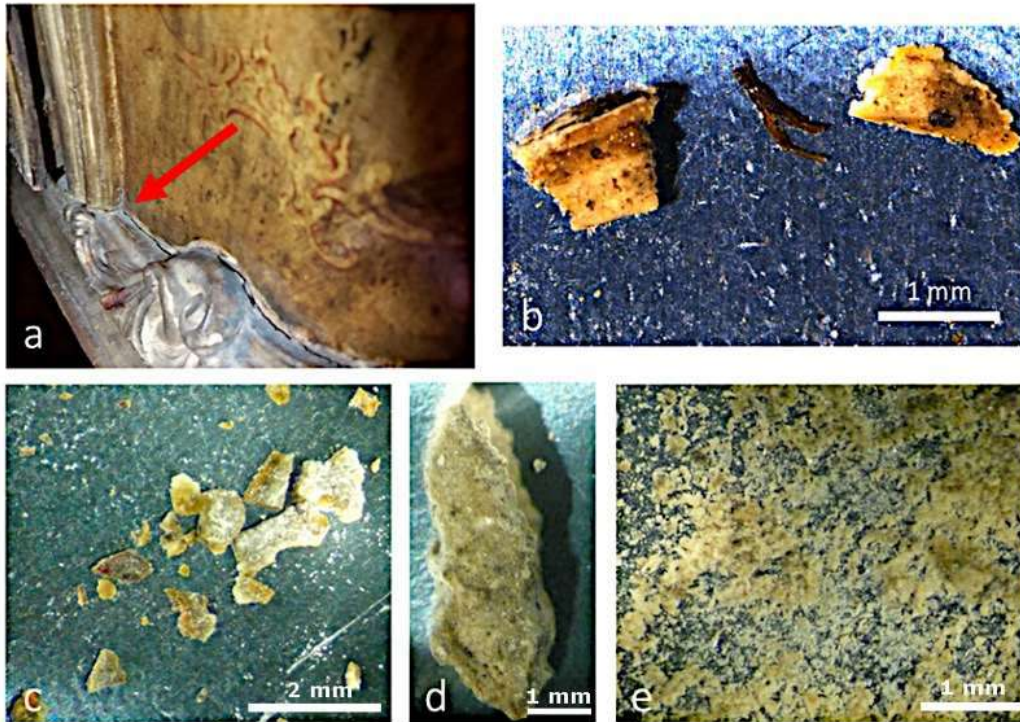


Figure 80. (left) The golden sample MGD138 taken on the left bottom corner of a central door of the golden Berlin carriage (CMV64.002-2), (right) picture of the sample under binocular microscope (GifA20354)

Radiocarbon results (Figure 81 and 82, Table 26)

The MGD138 sample taken from the bottom left corner of a central door of the golden Berlin carriage (CMV64.002) was split into 3 parts:

- Sample GifA20354.1 (MGD138) from the upper coats with shellac. It was treated as a bulk sample, and combusted under O₂ in the micro-line. It yielded the intervals [1956 – 1957] and [2011 – 2016]. As nothing was applied on the sled during the 21st c., we can restrict the possibilities to the [1956 – 1957] interval. This result is compatible with an intervention by Brigadier Piéri in the 1960s, when a varnish with compounds contemporary with this restoration such as linseed oil was applied.
- Sample GifA20354.2 from the central coats was thermally treated using 2 temperature steps. It was assumed that the fraction [0-300°C] (GifA20354.2.1) would represent the age of the varnish comprising carbons from "volatile" organic ingredients and carbons contemporary with the making of lead white.

The fraction [300-920°C] (GifA30354.2.2) provides information on the contamination by geological carbons from lead white.

The high temperature fraction provided CO₂ in much higher amounts than the low-temperature fraction (99 µgC vs. 7 µgC) and showed a low ¹⁴C content (¹⁴C age: 8825 ± 80 BP) that confirms the presence of geological carbons from lead white in this subsample. The low temperature fraction provided the range of dates: [1958 – 1959], [1986 – 1986] and [1987 – 2001]. Again, we favour the [1958 – 1959] interval and associate it with the action of Brigadier Péri, around the 1960s.

- Sample GifA20354.3 from the lower preparation coat was thermally treated using three temperature steps: the [0-300°C] fraction (GifA20354.3.1), which should represent the

age of the varnish, the [300-400°C] fraction (GifA20354.3.2) to evaluate the impact of this new threshold at 300°C (cf. the dragon sled), the [400-920°C] fraction to evaluate the content in geological carbons. The [0-300°C] and [300-400°C] steps did not produce enough CO₂ to assess the carbon content or the ¹⁴C content. The high temperature fraction provided enough CO₂ (19µgC) for measurement and confirmed the presence of geological carbons from lead white in the preparation coat with a ¹⁴C age of 2930 ± 90BP.

The ¹⁴C results on the MGD37 sample taken on the bottom left side of a central door of the golden Berlin carriage (without the preparation layer (CMV64.001), provided the following range of dates: [1045 – 1086] (10.1%), [1094 – 1105] (1.6%) and [1120 – 1280] (83.7%). This low ¹⁴C content could be due to a mixture of the original varnish ingredients, geological carbons (F¹⁴C=0) from the lead white (possibly present in trace amounts) and renovation with products from the 1960s contemporary with the bomb peak (F¹⁴C ≫ 1). However, before combustion under oxygen, the sample underwent an acid treatment which resulted in the elimination of traces of carbonate, especially geological ones. This low ¹⁴C content should thus be compared to our results for the eagle sled (CMV57.006). Again, we can only assume contamination by restoration products containing petroleum-derived ingredients.

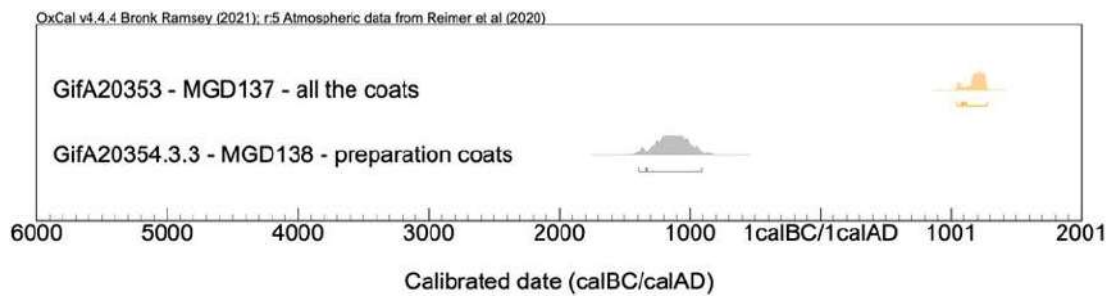


Figure 81. Calibrated range of dates using the post-bomb atmospheric NH1 curve on the MGD138 samples of the coating layers of the golden Berlin carriage (CMV64.002) (Hua et al. 2021).

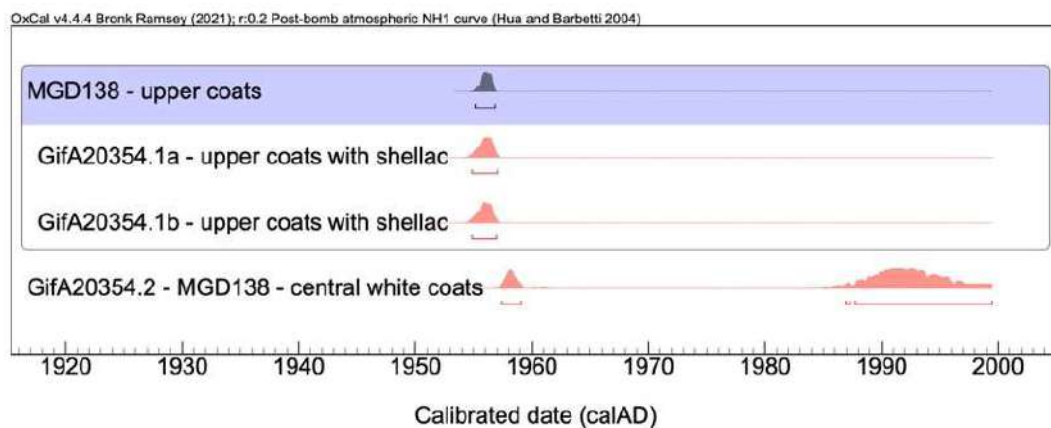


Figure 82. Calibrated range of dates using the post-bomb atmospheric NH1 curve on the MGD138 samples of the coating layers of the golden Berlin carriage (CMV64.002) (Hua et al. 2021, 2004).

Table 26. ¹⁴C results on the MGD137 and MGD138 samples of the coating of the Berlin carriage CMV64.002. The CO₂ was produced on the micro-line and the cracking-GIS was used as the interface to introduce the CO₂ into the ECHO MICADAS gas source. Calibration was done using IntCal20 (Reimer et al. 2020) and post-bomb calibration 2021 (NH1 zone, Hua et al. 2021) thanks to the OxCal v4.4 software (Bronk Ramsey).

sample ID				Description	Chemistry	Mass [µgC]	raw data				processed data		
N° inv.	MGD ID	Chemistry ID	measurement ID				F ¹⁴ C	±	year [BP]	±	Acomb / An	IntCal20 and Bomb21 cal. ranges [AD] (95% proba)	
CMV64 002-1	MGD137	GifA20353	ECHO-3953.1.2	Upper layers without preparation coat – metal leaves and binders	A	86	0.9011	0.0064	840	60		[1045 – 1086] (10.1%) [1094 – 1105] (1.6%) [1120 – 1280] (83.7%)	
CMV64 002-2	MGD138	GifA20354.1a	ECHO-3953.1.3	upper coats with shellac	A	74	1.0342	0.0075			123.7 /50.0	[1955.7 – 1956.6] (15.0%) [2011.1 – 2015.9] (80.4%)	
		GifA20354.1b	ECHO-3954.1.1			61	1.0325	0.0072					
		GifA20354.2.1	ECHO-3999.1.1	central white coats, metal leaves, oil binder	Thermolysis (T<300°C)	7	1.1448	0.0238				[1957.8 – 1959.1] (7.7%) [1986.1 – 1986.4] (0.6%) [1986.7 – 2000.6] (87.2%)	
		GifA20354.2.2	ECHO-3999.1.2		Thermolysis (300°C- 920°C)	99	0.3333	0.0034	8 825	80	-		
		GifA20354.3.1	-	lower preparation coats	Thermolysis (T<300°C)	no gas							-
		GifA20354.3.2	-		Thermolysis (300°C-400°C)	no gas							-
		GifA20354.3.3	ECHO-3999.1.3		Thermolysis (T>400°C)	23	0.6945	0.0077	2 930	90			

6.4.5. Sedan chair, inv. CMV78, coll. MNVT

Material history of the object

The sedan chair CMV.78 owned by the Musée de Cluny has been on loan to the Château de Compiègne since 1936 and little is known about its provenance. The body is painted with decoration on a gilded background usually named "verniss Martin".

Sampling location (Figure 83 and Figure 84)

The CMV78-1 sample was taken (MGD139, GifA20355):

- brush hair stuck on the décor of one of the doors from an intervention in the 1960s.

The CMV78-2 sample was taken (MGD140, GifA20356):

- Run of brown varnish decor of one of the doors, likely from the 1960s intervention.

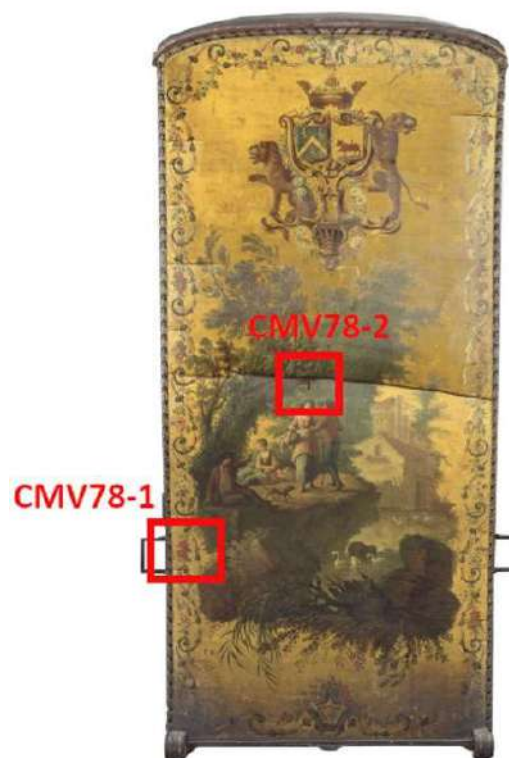


Figure 83. Location of the samples CMV78-1 and -2 on the sedan chair, c. 18th c. (inv CMV78, © MNVT, Compiègne)



Figure 84. (from left to right) Location of the MGD139 and MGD40 samples on the sedan chair (CMV78-1 and-2)

Table 27. ^{14}C results on the MGD139 and MGD140 samples of the sedan chair CMV78. The CO_2 was produced on the micro-line and the cracking-GUS was used as the interface to introduce the CO_2 into the ECHO MICADAS gas source. Calibration was done using IntCal20 (Reimer et al. 2020) and Bomb21 (NH1, Hua et al. 2021) thanks to OxCal v4.4 (Bronk Ramsey 2009).

sample ID				Description	Chemistry	Mass [μgC]	raw data				processed data		
N° inv.	MGD ID	Chemistry ID	measurement ID				F^{14}C	\pm	year [BP]	\pm	IntCal20 and Bomb21 cal. ranges [AD]	Acomb/An	IntCal20 and Bomb21 cal. ranges [AD]
CMV78-1	MGD139	GifA20355	ECHO-3816	brush hair	-	34	1.1159	0.0119			[1957.7 – 1958.6] (7.2%) [1992.0 – 1992.4] (1.3%) [1992.8 – 2000.9] (86.9%)		
CMV78-2	MGD140	GifA20356	ECHO-3817	upper brown varnish on the decor of one of the doors	-	70	0.9627	0.0076	305	65	[1446 – 1680] (89.9%) [1740 – 1752] (0.8%) [1762 – 1800] (4.7%)	53.0/50.0	[1650 – 1695] (39.0%) [1726 – 1811] (42.5%) [1839 – 1842] (0.2%) [1873 – 1878] (0.3%) [1917.5 – 1954.0] (13.4%)
							After(1650AD)						

Radiocarbon results

The ^{14}C measurements of the MGD139 sample taken on a brush hair stuck on the surface varnish yielded the range of dates: [1957 – 1958] (6.6%) and [1994 – ...] (88.8%), consistent with a brush used in the 1960s (Table 27).

The run of varnish provided the following range of dates after ^{14}C measurements: [1446 – 1680] (89.9%), [1740 – 1752] (0.8%) and [1762 – 1800] (4.7%). This might appear as contradicting a supposed intervention in the 1960s and, on the contrary, appear as consistent with an original "slip-up" of the 18th c. But this hypothesis does not seem reasonable. How could the brush hair from 1960 be found in a layer from the 18th c. And, indeed, combining the F^{14}C with a constraint that is assumed to reveal only intervals compatible with the 18th century ("after(1650)" function), revealed several new intervals, the most recent of which could indeed be compatible with a restoration phase in the 1960s: [1918 – 1956] (Figure 85).

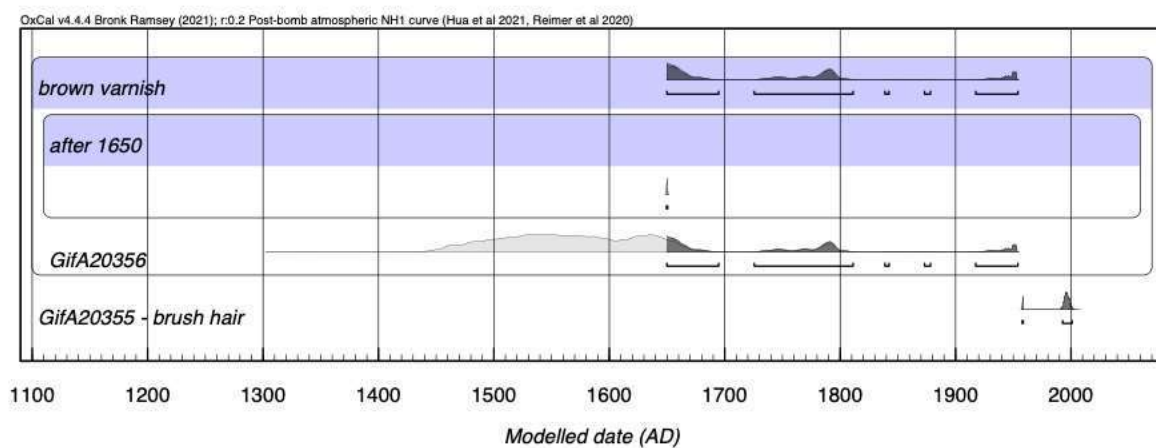


Figure 85. Calibrated range of dates using IntCal20 on the MGD139 and MGD140 samples of the coating layers of the sedan chair (CMV78) (Reimer et al., 2020)

6.4.6. Red and gold sled, inv. TR1868, coll. RMAH

Material history of the object

The red and gold sled TR1868 was made in Antwerp in the early 18th c. according to RMAH archives. The decoration is based on the blend of Asian and European tastes imitating a style developed by French painters as Paris had a great influence on decorative arts in Europe until the late 18th c. (Decq et al., 2019). The stratigraphy is original. However, a wax layer was applied in the 1980s as for several carriages from the collection.

Sampling location (Figure 86)

The samples TR1868-1 and TR1868-2 were taken from the flaked coats under the left side of the red and gold sled. The stratigraphy of the coating is original comprising (Figure 86): 1- preparation coats with a blue layer of Prussian blue, 2- red coats with successively a layer of vermilion and a layer of carmine, 3- oil/resin mixtion, 4- gold leaf, 5- carmine coat. The surface was scraped as carefully as possible before sampling to remove a protective wax or paraffin layer applied in the 1980s.

The sampling campaign was based on the knowledge and expertise acquired by members of the ELinC project.

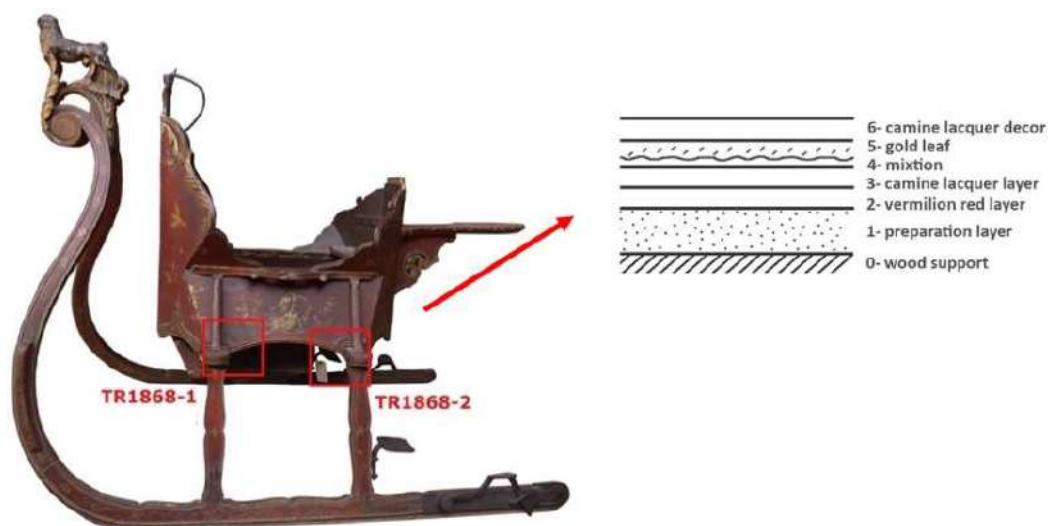


Figure 86. Location of the samples TR1868-1 and -2 on the red and gold sled, 18th c., Antwerp (inv. TR1868, ©KMKG-RMAH, Brussels) (long. 130 cm x large 153 cm x hight 98 cm,

Material characterization

The collection of sleds at the Royal Museums of Art and History (RMAH) was studied with the partnership of the Royal Institute for Cultural Heritage (KIK- IRPA) and the University of Antwerp (UA) during the ElinC project (2012-2018) in order to acquire deeper knowledge of the technological history of European lacquers. Thanks to the exchanges with Emile Van Binnebeke, Louise Decq and Vincent Cattersel, it was possible to have a complete organic and inorganic characterization layer by layer of the coating stratigraphy of the sleds.

The stratigraphy comprises 15 layers containing drying oil, wax and Pinaceae resin, Prussian blue, lead white, minium, earth pigments, vermilion and alum associated with carmine lake (Decq et al., 2019) (Figure 87). A priori, except for Prussian blue, the binders and pigments detected by SEM-EDS and Py-GC-MS at KIK-IRPA are not expected to be contaminants of ¹⁴C measurements after A chemical treatments.



Figure 87. Stratigraphy performed by Louise Decq KIK-IRPA (figure adapted from unpublished report, KIK-IRPA, KMKG-MRAH © ElinC project) – Red and gold sledTR1868 (© KIK-IRPA / RMAH-KMKG, Brussels)

Sub-sampling

The sample MGD146 (Figure 88) was observed under binocular microscope. Due to the friability of the sample, it was decided to perform ¹⁴C dating on the bulk sample without separating the

lower blue and white preparation coats (PbO, Prussian blue) from the upper red coats (HgS, red lake) (GifA20361).



Figure 88. Sample location for ^{14}C dating on the red and gold sled (TR1868-1), coll. KMKG-MRAH. Pictures taken by Marie-Gabrielle Durier and Louise Decq. (right) Picture of the MGD146 sample under binocular microscope (GifA20361)

MGD147 (Figure 89) was observed under binocular microscope. It comprises powder of the blue preparation layer with some chips of the red coats which were separated using microchisels:

- Powder with Prussian blue collected in a glass tube under UV light (GifA20362.1)
- Chips of red coats separated from the blue powder under binocular microscope (GifA20362.2)



Figure 89. Sample location for ^{14}C dating on the red and gold sled (TR1868-2), coll. KMKG-MRAH. Pictures taken by Marie-Gabrielle Durier and Louise Decq.

Radiocarbon results (Table 28, Figure 90)

The underlying blue preparation layer (GifA20362.1) yielded the following ranges of dates: [774–787] (1.4%), [829–857] (2.4%), [872–1048] (86.6%), [1083–1129] (4.2%), [1038–1150] (0.9%). The ageing of the blue sample might not be due to contamination by the preparation layer (chalk/lead white) from which carbons are removed during the A treatment. However, the ageing could be induced by the presence of carbonates linked to cyanide with 3 covalent bonds in Prussian blue; the cyanide bonds $\text{C}\equiv\text{N}$ might not be attacked using an A chemistry protocol. The production processes of Prussian blue need to be investigated to find the origin of the added carbon, which could be organic or geological depending on the suppliers (Chapter 2 – § 4.2.2.2). If the added carbon is of geological origin, it could resist the A chemistry protocol and this residue could have aged the ^{14}C dating of the sample.

Table 28. ^{14}C results on the MGD146 and MGD147 samples of the coating layers of the red and gold sled TR1868. The CO_2 was produced on the micro-line and the cracking-GIS was used as the interface to introduce the CO_2 into the ECHOmicADAS gas source. Calibration was done thanks to OxCal v.4.4 (Bronk Ramsey, 2009) using IntCal20 (Reimer et al. 2020).

sample ID				Description	Chemistry	Mass [μgC]	raw data				Acomb/ An	processed data
N° inv.	MGD ID	Chemistry ID	measurement ID				F^{14}C	\pm	year [BP]	\pm		
TR1868-1	MGD146	GifA20361	LOST	red and blue coats	A	-	-	-	-	-	-	-
TR1868-2	MGD147	GifA20362.1	ECHO-3741.1.3	Prussian blue coat	A	62	0.875	0.006	1 070	55		[774–787] (1.4%) [829–857] (2.4%) [872–1048] (86.6%) [1083–1129] (4.2%) [1038–1150] (0.9%)
		GifA20362.2a	ECHO-3741.2.1	upper red coats	A	114	0.950	0.007	420	55	111.5 / 50.0	[1436–1526] (64.0%) [1556–1632] (31.5%)
		GifA20362.2b	ECHO-3741.2.2			89	0.954	0.006	380	55		

The upper red coats (GifA20362.2) provided the ranges of dates: [1436–1526] (64.0%), [1556–1633] (31.5%) with a high Acomb value of 111.5%. This result is older than the expected early 18th c. An initial assumption was that traces of Prussian blue had contaminated the sampling of the red coat. However, 30% of Prussian blue would have been needed to explain the measured shift from the F¹⁴C of the 18th century (F¹⁴C ~ 0.95); this ratio is high for eye detection between blue and red using a binocular microscope. A more reliable explanation is the impact of the upper protective wax or paraffin film applied in the 1980s despite careful scraping to get rid of the restored surface. Impregnation by these products containing dead carbons (F¹⁴C = 0), resulting in only 3% of the final measured carbons, can explain the aging we observed.

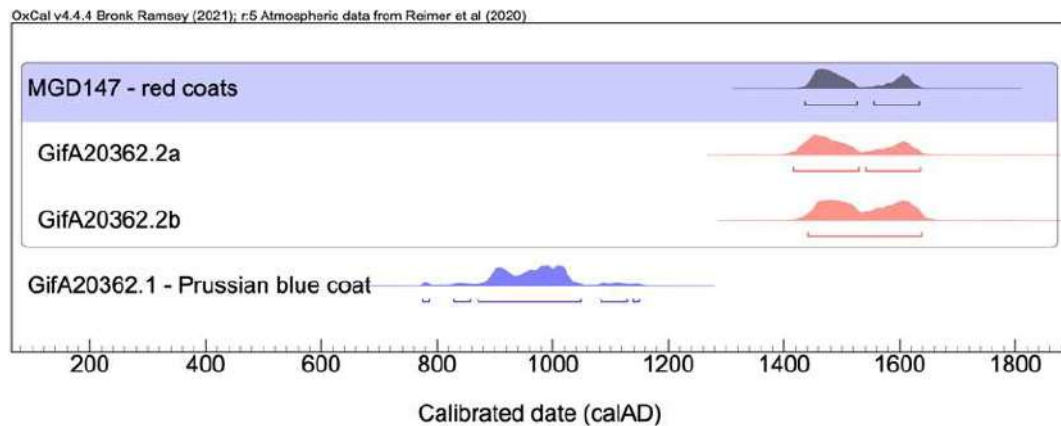


Figure 90. Calibrated range of dates using IntCal20 on the MGD147 samples of the blue and red coats of the red and gold sled TR1868 (Reimer et al., 2020).

6.4.7. Tortoise shell and silver leaf sled, inv. TR88, coll. RMAH

Material history

The tortoise shell and silver leaf sled TR88 is estimated to have been made in Liège during the second half of the 18th c. (?). The original layers correspond to the first blue decoration. It is stylistically assumed that the second brown decoration was applied during the early 19th c. in order to cater to new aesthetic tastes. The techniques of imitating tortoise and marble were already present in Europe before the beginning of Asian lacquer imitations. The study of this sled could provide information on the appropriation of eastern lacquering practices by European craftsmen (Decq et al., 2019). Finally, a wax layer was applied in the 1980s as for several carriages from the collection.

Sampling location (Figure 91)

The MGD142, MGD143, MGD144 were taken from a single stratigraphy at the back right of the body of the sled under a top moulding (TR88-1). The stratigraphy (Figure 91) comprises two decorative layers applied successively at different periods:

- 1- blue white preparation coats (lead white, Prussian blue),
- 2- original blue décor (c.1750?)
- 3- brown decor (early 19th c.?)
- 4- wax restoration layer



Figure 91. Location of the sample TR88-1 on the tortoise shell and silver leaf sled, second half of the 18th c., Liège (inv. TR88, © KMKG-RMAH, Brussels) (long. 116 cm x large 179 cm x hight 88 cm)

During the sampling for ¹⁴C dating, the surface was scraped as carefully as possible to avoid contamination of the original preparation layer by recent non original layers.

Material characterization

In the framework of the ELinC project, analyses revealed ten layers in the stratigraphy containing silver leaf, lead white, earth pigment, Prussian blue, lamp black, minium, and beeswax (Decq et al., 2019). Analysis was performed with SEM-EDS at KIK-IRPA (Figure 92). Except for Prussian blue, whose carbon may be of geological or biological origin, the other pigments should not induce ¹⁴C contamination.

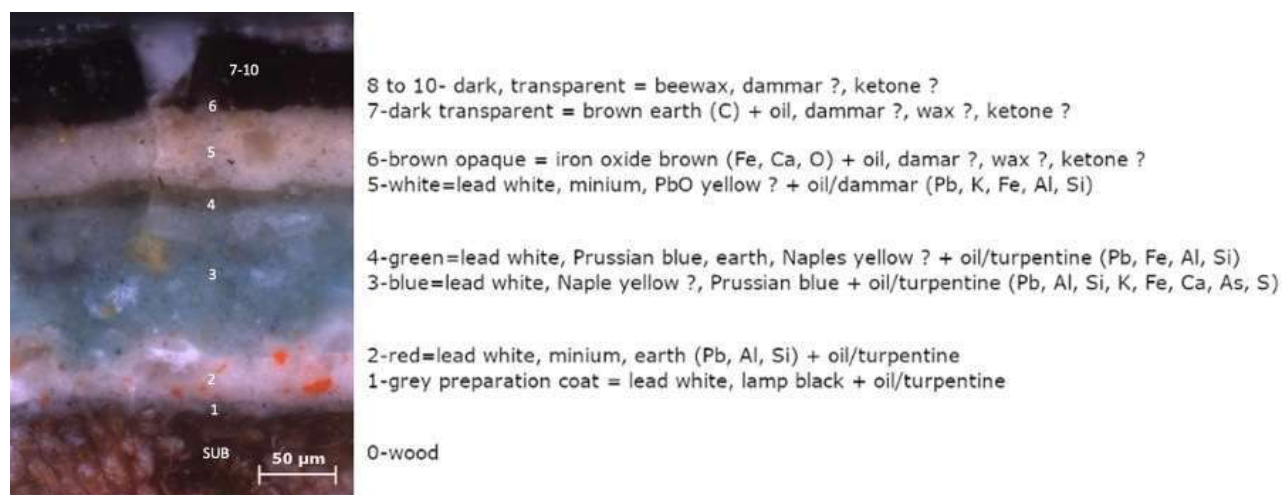


Figure 92. Stratigraphy performed by Louise Decq KIK-IRPA (figure adapted from unpublished report, KIK-IRPA, KMKG-MRAH © ELinC project) - Tortoise shell and silver leaf sled TR88 (© KIK-IRPA / RMAH-KMKG, Brussels)

On the same sampling localization for ¹⁴C dating, an additional sub-sample comprising the blue preparation layer and surface restoration treatments was analyzed using Py-GC-MS at KIK-IRPA. It revealed the presence of: drying oil, rapeseed oil, protein, gum (?), ketone varnish, trace of dammar (?), and degraded Pinaceae resin.

Sub-sampling

The chips of blue and brown layers of the blue and brown decors (samples MGD142 and MGD143) could not be properly separated using microchisels *in situ*, due to the strong adhesion

between the first and second decor. Separation could not be performed in the laboratory under binocular microscope due to the high friability of the samples. Thus, they were kept in storage for ^{14}C dating.

Sample MGD144 was collected in a glass tube. It corresponds to the preparation coat under the samples MGD142 and MGD143 (blue and brown decors) and contains lead white and grains of Prussian blue that could not be separated (GifA20359) (Figure 93).



Figure 93. Location of the MGD142, MGD143 and MGD144 samples for ^{14}C dating on the red and gold sled (TR88-1), coll. KMKG-RMAH

Radiocarbon results (Table 29, Figure 94)

The lower preparation coats with lead white and Prussian blue provided the following ranges of dates: [1459 –1683] (83.6%), [1736 –1803] (10.6%) and [1936 – ...] (1.2%) (Table 29, Figure 29). The interval [1736 –1803] (10.6%) yielded by ^{14}C dating of the original preparation coats is consistent with the manufacturing date c.1750 assumed by museum experts. It is interesting to note that unlike the TR1868 sled, the presence of Prussian blue does not seem to have aged the preparation layer. We saw previously that this pigment can have several origins (geological and biological). Here, the carbons might be of a biological origin corresponding to the making period of the sled. This result may inform us on the methods of obtaining this blue pigment.

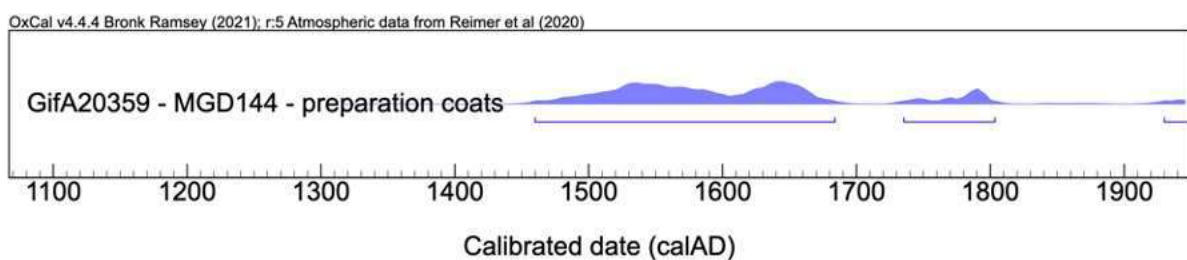


Figure 94. Calibrated range of dates using IntCal20 on the MGD144 sample of the blue white preparation coats of the tortoise shell and silver leaf sled TR88 (Reimer et al., 2020)

Table 29. ^{14}C results on the MGD142, MGD143 and MGD144 samples of the coating layers of the tortoise shell and silver leaf sledTR88. The sample processing includes CO_2 obtention and purification in the μ line and introduction in the gas source of ECHoMICADAS through the cracking-GIS device. Calibration was done on IntCal20 (Reimer et al. 2020) thanks to OxCal4.4 software (Bronk Ramsey, 2009).

sample ID				Description	Chemistry	Mass [μgC]	raw data				processed data
N° inv.	MGD ID	Chemistry ID	measurement ID				F^{14}C	\pm	year [BP]	\pm	IntCal20 cal. ranges [AD] (95% proba)
TR88-1	MGD142	GifA20357	-	sled back right - inseparable brown and blue decors							
	MGD143	GifA20358	-	sled back right - inseparable brown and blue decors -							
	MGD144	GifA20359	ECHo-3740	sled back right – preparation coats	A	121	0.966	0.007	280	55	[1459 - 1683] (83.6%), [1736 - 1803] (10.6%) [1936 -...] (1.2%).

6.4.8. Aventurine sled, inv. TR41, coll. RMAH

Material history

As for the other sleds, little documentation subsists on the material history of the Aventurine sled TR41 which is assumed to have been made in Paris in a Louis XV style during the second half of the 18th c.⁵¹. This style was partly identified by experts based on the gilded rococo frame, the original Aventurine decoration and gilded sunrays. The original decoration was overpainted with dark decoration to cater to new aesthetic tastes during the 19th c. A wax layer was applied in the 1980s as on several carriages from the collection (Decq et al., 2019).

Sampling location (Figure 95)

The MGD145 sample was taken from the back right of the body of the sled under a top moulding (TR41-1). The stratigraphy comprises two decorative layers applied successively at different periods: 1- white and pink preparation coats (vermillion, chalk, lead white), 2- original Aventurine coats (c.1750?), 3- black decor (19th c.?), 4- wax restoration layer (Figure 95).

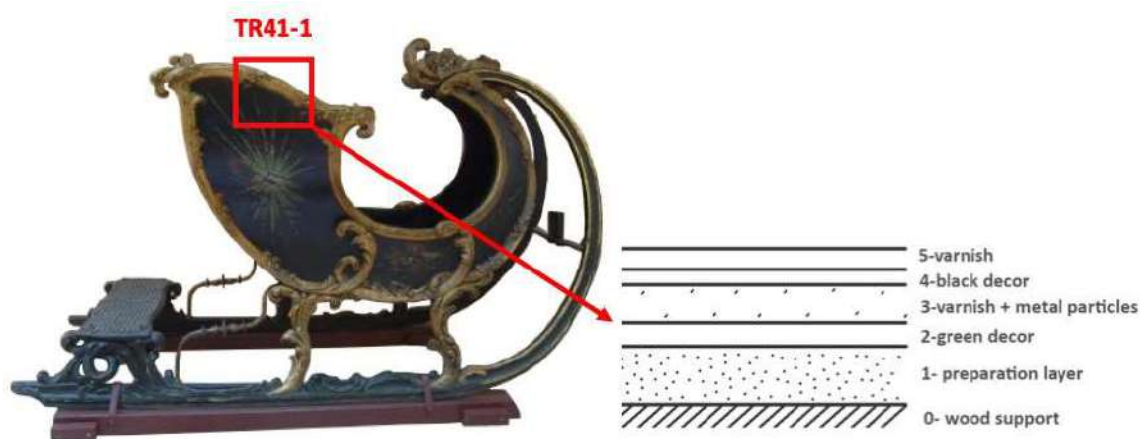


Figure 95. Location of the sample TR41-1 on the Aventurine sled, Louis XV style, by 1750 (inv. TR. 41, ©KMKG-RMAH, Brussels) (long. 212 cm x large 102 cm x hight 125 cm).

Material characterization

The stratigraphy of the MGD45 sample is deducible from the material analyses performed at the KIK-IRPA using SEM-EDS and Py-GC-MS in the framework of the ELinC project. 22 layers were identified comprising the Aventurine decor (Figure 96).

The original Aventurine organic layer from the 18th c. contains copper particles and a mixture of Prussian blue, verdigris, Naples yellow or lead tin yellow, chalk and aluminium grains in an organic binder made of drying oil, colophony and traces of copal and shellac.

The black overpaint layer from the 19th c. is made of carbon black with oil, copal and colophony. The surface is again covered by a transparent layer, possibly a styrene-acrylic copolymer varnish. Some beeswax was also detected on the surface layers; it is probably due to a restoration layer applied on the sleds of the MRAH collection in the 1980s.

⁵¹ Unpublished report : Decq, L. (2017). *Black and green sled with Aventurine decoration* (European Lacquer in Context Project (ELinC) 2017.13437). KIK-IRPA.



- 13-18- dark, transparent = beeswax, soot, oil, pine resin, Congo copal ?, ketone ? shellac ?
- 12-black = (Cu) + oil, pine resin, copal, styrene
- 5-11-transparent = (Cu) + oil, copal, pine resin
- 4-green = lead white, Prussian blue, Naples yellow ? + oil/turpentine, shellac ?
- isolation layer = shellac ?
- 3-pink = lead white, vermilion, chalk + oil/turpentine, shellac ?
- 2-white = lead white, minium, chalk (Pb, Ca, Al, Si) + oil/turpentine
- 1-preparation coat = chalk + protein glue
- 0-wood

Figure 96. Stratigraphy on the Aventurine sled TR41 (figure adapted from unpublished report KIK-IRPA, KMKG-RMAH ©ELinC project)

The MGD145 sample was taken under a top moulding (TR41-1) after removal of the black overpaint layer with microchisels. The sample was observed under binocular microscope (GifA20360) (Figure 97).

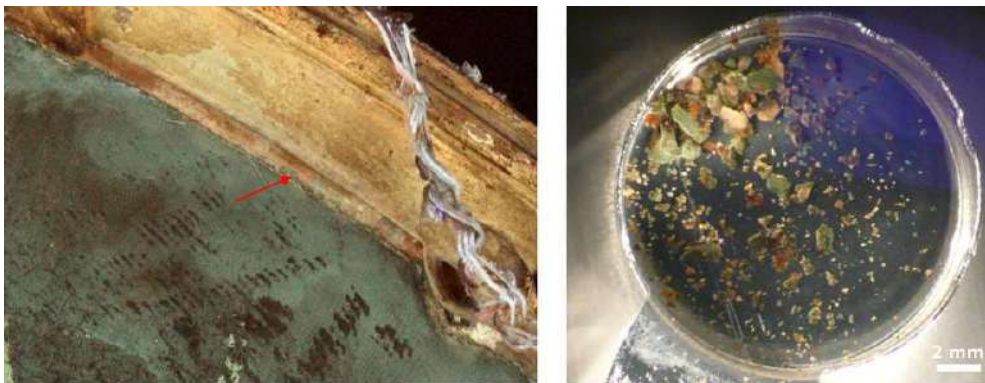


Figure 97. Location of the MGD145 sample for ¹⁴C dating on the Aventurine sled (TR41-1)

Radiocarbon results (Table 30)

The original Aventurine decor provided the following ranges of dates: [76 - 215] (95.4%) (Table 30). Since the black layer and those above it have been removed, it is unlikely that the apparent aging is the result of the restoration products that were applied in the 1980s. The presence of lead white in the analyzed layers cannot be invoked either, since the A treatment leached these geological carbons. The presence of Prussian blue, which is resistant to acid leaching, could explain this aging. However, the ageing effect is much greater here than it was for TR1868. The use of copal remains the most likely hypothesis. Indeed, the presence of this subfossil copal is consistent with this marked ageing and also with the large mass of carbon (792 μg) extracted. Such a quantity cannot be explained with Prussian blue as the unique source of carbon.

Table 30. ¹⁴C results on the MGD145 sample of the coating layers of the Aventurine sled TR41. The sample processing included CO₂ extraction and purification in the μ line, CO₂ reduction in "Gégé" and introduction in the solid source of ECHoMICADAS. Calibration was done on IntCal20 (Reimer et al. 2020) thanks to OxCal4.4 software (Bronk Ramsey, 2009)

sample ID				Description	Chemistry	Mass [μ gC]	raw data				processed data
N° inv.	MGD ID	Chemistry ID	measurement ID				F ¹⁴ C	±	year [BP]	±	IntCal20 cal. ranges [AD] (95% proba)
TR41-1	MGD145	GifA20360	ECHo-3745.1.1	green and preparation coats	A	792	0.790	0.002	1 900	20	[76 - 215] (95.4%)

6.5. Gut strings of musical instruments

Samples of gut strings (coll. Musée de la musique) were taken on several stringed instruments:

- Gut string samples MGD20 from a Tielke lute, c.1690, Historisches Museum Frankfurt⁵².
- Gut string samples MGD19 from a lute, Brunner, 1764, coll. Narod Museum, Prague⁵³.
- Gut string samples MGD32 from a Gabrielli violin, 1769, private coll. atelier Cels.
- Gut string samples MGD18 from a Bernardel cello n°506, 1896, Paris, coming from the private coll. Bernard Millant 2012 and sold unused at the Vichy Auction in 29th November 2017, batch n°70.

6.5.1. Gut strings of the Tielke lute

Material history of the object

The samples are from a gut string of the Tielke lute, c.1690 (coll. Historisches Museum Frankfurt) (Figure 98). According to the visual examination of museum experts, these strings appear to be from the pre-industrial period (17th or 18th c.), without being able to date them accurately.



Figure 98. A gut string of the lute Tielke, c.1690, coll. Historisches Museum Frankfurt.

⁵² Friedemann Hellwig, Barbara Hellwig, Joachim Tielke: *Kunstvolle Musikinstrumente Des Barock*, 2011, p.121.

⁵³ *Les instruments de musique à travers les âges*, Paris 1972, illustration 151-152.

Table 31. ¹⁴C results of gut strings from the lute, Tielke, 1690, coll. Historisches Museum Frankfurt. The sample processing includes CO₂ extraction, urification and reduction in AGE3 and introduction in the solid source of ECHOmicADAS. Calibration is done on IntCal20 (Reimer et al. 2020) thanks to OxCal4.4 software (Bronk Ramsey, 2009).

sample ID				Chemistry	Mass [μgC]	raw data				processed data			
Instrument	MGD ID	Chemistry ID	measurement ID			F ¹⁴ C	±	year [BP]	±	Acomb /An	IntCal20 cal. ranges [AD] (95% proba)	Acomb /An	IntCal20 cal. ranges [AD] (95% proba)
Lute, Tielke, c.1690, Historisches Museum Frankfurt	MGD20	GifA19193.1	ECHO-3311.1.1	DCM x 3	847	0.9786	0.0024	175	20	121.9 /40.8	[1667 – 1685] (18.2%) [1732 – 1782] (53.4%) [1796 – 1804] (6.4%) [1927 - ...] (17.4%)	116.5 /31.6	[1773 – 1781] (84.8%) [1797 – 1804] (10.6%)
		GifA19193.2	ECHO-3311.1.2	DCM x 3	672	0.9773	0.0022	185	20				
		GifA19193.3	ECHO-3311.1.3	DCM/MeOH/Ac	657	0.9793	0.0022	170	20				
											After(1690AD) Before(1900AD)		

Radiocarbon results (Table 31, Figure 99)

The ^{14}C results are statistically compatible at 1σ no matter which chemical treatment is applied. The combination of the ^{14}C measurements yielded the following intervals with a high A_{comb} of 121.9%: [1667-1685] (18.2%), [1732-1782] (53.4%), [1796-1804] (6.4%), [1927-...] (17.4%) (Table 31).

Adding the lute manufacture year (1690AD) as *terminus post quem*, and the 1900AD as *terminus ante quem* to exclude the impact of the Suess effect restricts the potential intervals to [1733-1781] (84.8%) and [1797–1804] (10.6%) (Table 31, Figure 99).

This result agrees with a last replacement of the strings during the second half of the 18th c.

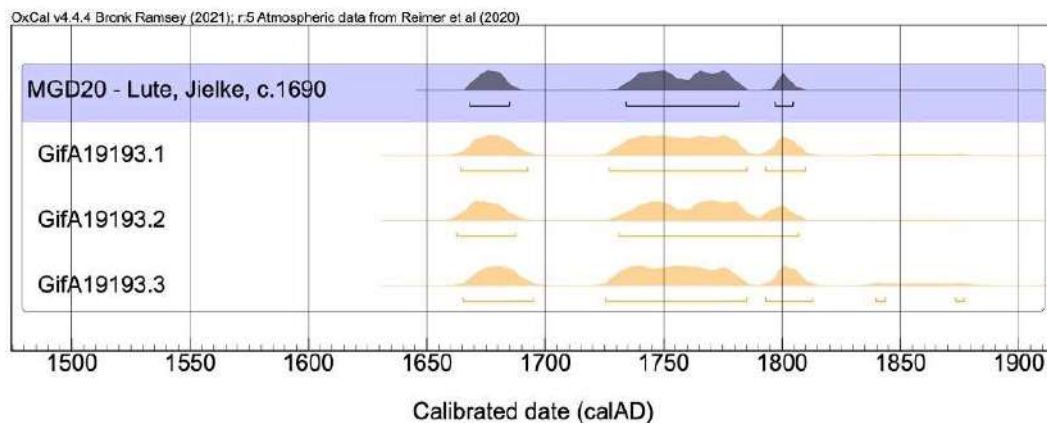


Figure 99. Calibrated range of dates using IntCal20 on the sample MGD20 from an original gut string of a lute, Tielke, c.1690, coll. Historisches Museum Frankfurt (Reimer et al., 2020)

6.5.2. Gut strings of the Brunner lute

Material history of the object

Samples were taken on gut strings disassembled from a lute, Brunner, 1764 (coll. Narod Museum, Prague) (Figure 100). According to the visual examination of museum experts, these strings appear to be from the pre-industrial period (17th or 18th c.).



Figure 100. An original gut string of the lute, Brunner, 1764, coll. Narod Museum, Prague.

Radiocarbon results (Table 32, Figure 101)

The ^{14}C measurements on the gut strings of the lute, Brunner, 1764 (coll. Narod Museum, Prague) are reproducible despite different chemical treatments with a slightly higher

measured $F^{14}C$ for the sample treated with DCM/MeOH/Ac. The combination of the ^{14}C results yielded the intervals: [1662-1684] (24.9%), [1736-1804] (64.3%), [1936-...] (6.3%) with an Acomb value of 97.8%, i.e. higher than the 40.8% threshold (Table 32, Figure 101).

Adding the lute manufacture year (1764) as *terminus post quem*, and the 1900AD as *terminus ante quem* to exclude the impact of the Suess effect restricts the potential intervals to [1764-1786] (73.3%) and [1792-1801] (22.1%). The statistical agreement coefficient is high, 101.5% for a threshold at 31.6%. These intervals are in agreement with an original string and with a string replaced during the second half of the 18th c.

Table 32. ¹⁴C results of gut strings from the lute, Bunner, 1764, coll. Narod Museum, Prague. Sample processing include CO₂ extractions, purification and reduction in AGE3 and introduction in the solid source of ECHO MICADAS. Calibration was done on IntCal20 (Reimer et al. 2020) thanks to OxCal4.4 software (Bronk Ramsey, 2009).

Instrument	sample ID			Chemistry	Mass [μgC]	raw data				processed data			
	MGD ID	Chemistry ID	measurement ID			F ¹⁴ C	±	year [BP]	±	Acomb /An	IntCal20 cal. ranges [AD] (95% proba)	Acomb /An	IntCal20 cal. ranges [AD] (95% proba)
Lute, Bunner, 1764, Narod Museum, Prague	MGD19	GifA19192.1	ECHO-3313.1.1	DCM x 3	992	0.9754	0.0024	200	20	97.8 /40.8	[1662-1684] (24.9%) [1736-1804] (64.3%) [1936-...] (6.3%)	101.5 /31.6	[1763-1786] (73.3%) [1792-1801] (22.1%)
		GifA19192.2	ECHO-3313.1.2	DCM x 3	688	0.9749	0.0022	205	20				
		GifA19192.3	ECHO-3313.1.3	DCM/MeOH/Ac	656	0.9795	0.0023	170	20				
												After(1764AD) Before(1900AD)	

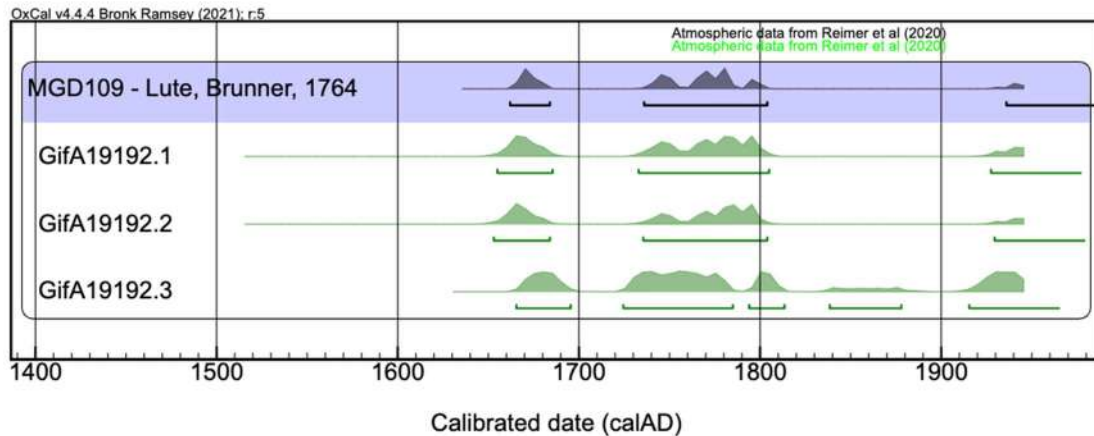


Figure 101. Calibrated range of dates using IntCal20 on the sample MGD19 from an original gut string of the lute, Brunner, 1764, coll. Narod Museum, Prague (Reimer et al., 2020)

6.5.3. Gut strings of a Battista Gabrielli violin

Material history of the object

The samples are from the gut string of a violin, Battista Gabrielli, 1769, private coll. atelier Cels (Figure 102). According to the visual examination of violin makers, these strings might have been changed at the end of the 18th c. or during the 19th c. with the pegs to maintain its playable condition without more precise clues to date them.



Figure 102. Gut string samples are from a violin Gabrielli, c.1769, private coll. Atelier Cels.

Radiocarbon results (Table 33, Figure 103)

The ¹⁴C measurements on the gut string sub-samples are shown in Table 34. They are reproducible whatever the chemical protocol applied as shown by a statistical agreement illustrated by a high Acomb value of 118.7%. The “combine option” in Oxcal provided the following range of dates: [1688-1730] (20.0%), [1806-1824] (8.1%), [1830-1894] (54.4%) and [1903-1924] (13.0%) (Table 33, Figure 103).

In view of the later modifications visible on the violin, this string may not be original. Thus, the [1688-1730] interval is not probable given the playing practices. The addition of 1769AD as *terminus post quem* (i.e. the date of the violin making) and 1900AD as *terminus ante quem*, to exclude the impact of the Suess effect, means that the possible intervals are restricted to [1808-1822] (12.4%) and [1831-1893] (83.2%). These intervals unfortunately cover the whole 19th c. However, they are compatible with the expected replacement of strings and pegs during the 19th c.

Table 33. ¹⁴C results on gut strings of the violin, Battista, 1716-71, coll. atelier Cels. Sample processing included CO₂ extraction, purification and reduction in AGE3 and introduction in the solid source of ECHoMICADAS. Calibration was done on IntCal20 (Reimer et al. 2020) thanks to OxCal4.4 software (Bronk Ramsey, 2009).

sample ID				Chemistry	Mass [µgC]	raw data				processed data			
Instrument	MGD ID	Chemistry ID	measurement ID			F ¹⁴ C	±	year [BP]	±	Acomb /An	IntCal20 cal. ranges [AD] (95% proba)	Acomb /An	IntCal20 cal. ranges [AD] (95% proba)
Violin, Battista Gabrielli, 1716-1771, Atelier Cels	MGD32	GifA19142.1	ECHo-3315.1.1	DCM x 3	987	0.9860	0.0024	110	20	118.7 / 40.8	[1688-1730] (20.0%) [1806-1824] (8.1%) [1830-1894] (54.4%) [1903-1924] (13.0%)	116.1 /31.6	[1808 – 1822] (12.3) [1831 – 1893] (83.2)
		GifA19142.2	ECHo-3315.2.1	DCM x 3	697	0.9844	0.0023	130	20				
		GifA19142.3	ECHo-3315.3.1	DCM/MeOH/Ac	604	0.9842	0.0022	130	20				

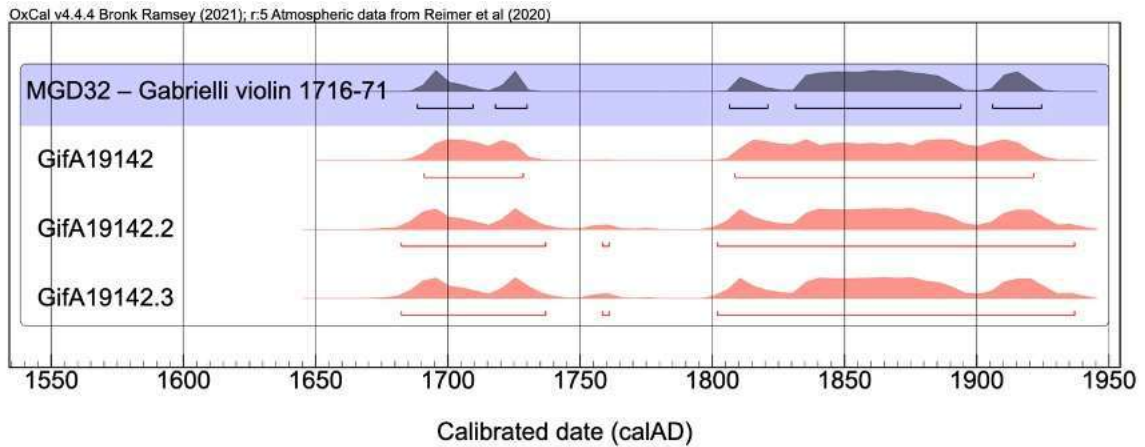


Figure 103. Calibrated range of dates using IntCal20 (Reimer et al., 2020) on the sample MGD32 from a gut string of a Gabrielli violin, 1716-71, coll. atelier Cels.

6.5.4. Gut strings of the Bernardel cello

Material history of the object

A gut string was sampled on a Bernardel cello n°506, 1896, Paris. Gustave Bernardel was a famous luthier in Paris (1832-1904). The cello has a label made for the Universal Exhibition in Brussels. The cello comes from the private coll. Bernard Millant 2012 and was sold unused with its original wires at the Vichy Auction on 29th November 2017, batch n°70. The bridge is original and signed by Bernardel. These tightly wrapped gut strings are typical of the period 1870-1900 in Paris according to museum expertise as shown by the comparison with a Baillot gut string from a violin, c. 1850 (Figure 104).



Figure 104. (from left to right) Sampling of an original gut string of the Bernardel cello, n°506, 1896. Gut string Baillot, violon c. 1850.

Radiocarbon results

The three string sub-samples give different $F^{14}C$ values depending on the protocol applied. The discrepancy between the results prevents their combination. The A_{comb} is much lower than the threshold ($30.6\% < 40.8\%$). The two DCM aliquots give statistically similar values at 0.968 ± 0.002 , 0.972 ± 0.002 whereas the DCM/MeOH/Ac aliquot gave a higher $F^{14}C$ at 0.977 ± 0.002 (Table 34, Figure 105).

All these results are in contradiction with the making period c.1896 as defined by the museum expertise which concluded that the strings are original and typical of Parisian strings between 1870 and 1900. Moreover, the cello bridge is original and signed by Bernardel. Bernardel's practice of reusing early strings is not a possible assumption.

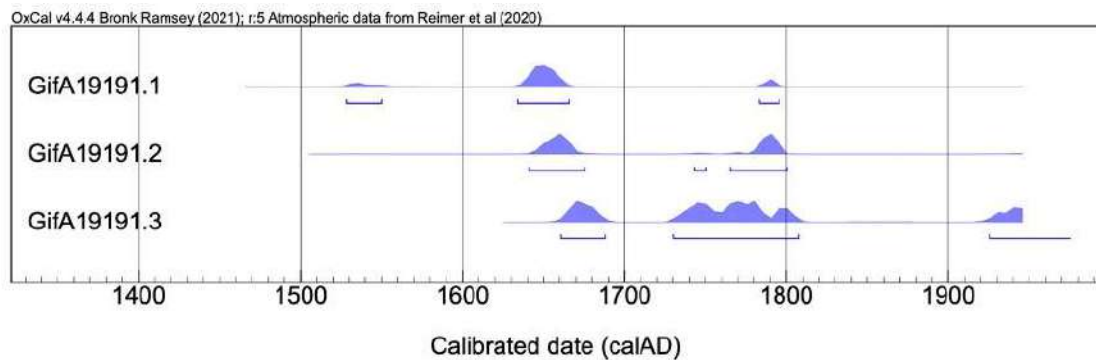


Figure 105. Calibrated range of dates using IntCal20 on the sample MGD18 from an original gut string of the cello, Bernardel n°506, 1896 (Reimer et al., 2020).

Table 34. ^{14}C results of gut strings from the cello, Bernardel n°506, 1896. The sample processing includes CO_2 extraction, purification and reduction in AGE3 and introduction in the solid source of ECHOMICADAS. Calibration was done on IntCal20 (Reimer et al. 2020) thanks to OxCal4.4 software (Bronk Ramsey, 2009).

sample ID				Chemistry	Mass [μgC]	raw data				processed data		
Instrument	MGD ID	Chemistry ID	measurement ID			F^{14}C	\pm	year [BP]	\pm	IntCal20 cal. ranges [AD] (95% proba)	Acomb /An	IntCal20 cal. ranges [AD] (95% proba)
Cello, Bernardel n°506, 1896	MGD18	GifA19191.1	ECHo-3314.1.1	DCM x 3	984	0.9683	0.0024	260	20	[1528-1549] (8.0%) [1634-1665] (81.7%) [1785-1795] (5.7%)	46.6 /40.8	[1653 – 1668] (41.9%) [1781 – 1798] (53.6%)
		GifA19191.2	ECHo-3314.2.1	DCM x 3	716	0.9719	0.0022	230	20	[1642-1673] (53.1%) [1769-1771] (0.6%) [1777-1800] (41.8%)		
		GifA19191.3	ECHo-3314.3.1	DCM/MeOH/Ac	757	0.9769	0.0022	190	20	[1661-1687] (20.7%) [1731-1807] (59.1%) [1926-...] (15.6%)		

The chemical CH_2Cl_2 treatment (polar aprotic solvent) was used to remove colophony and MeOH as a polar protic solvent dissolves proteins from fingerprints due to traces of use of gut strings. A future possibility could be to add cleaning with an apolar aprotic solvent such as hexane after or instead of the acetone step to remove highly apolar molecules such as hydrocarbons (bitumen) (Ferrant, 2021)(Figure 106).

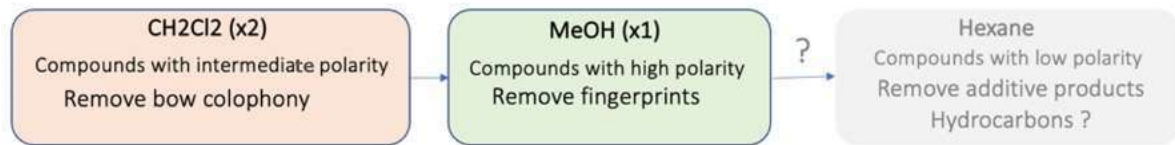


Figure 106. The chemical treatment for carbon decontamination of gut string samples (adapted from Ferrant, 2021).

Moreover, should we be concerned by interactions between the solvents and the gut components that would contribute to contaminating the strings with ^{14}C -free carbon? For example, gut strings naturally contain Fe(II) which progressively oxidizes into Fe(III) (Tsukamoto et al., 2020). Atmospheric CO_2 can react with Fe(II) to produce Fe-CO_3 during an alkali treatment. These ferrous carbonates require a final highly oxidative step to be released, so we can also point to the interactions with Fe(II) to explain contamination during the chemical step before ^{14}C dating (Hatté et al., 2001). This has also to be further investigated.

i- use practices

According to the storage and trade practices, early gut strings are traditionally assumed to have been made a few months before their placement on stringed instruments. The strings of the quartet are stretched close to the breakpoint value, so their duration of use is around from a few months to a few years depending on how the instrument is played (Chapter 1 – § 4.1). Lute gut strings are also changed very often. This confirms that the reuse of old strings is not an expected practice.

Another possible assumption is an interaction between the solvents used to clean colophony residues during playing practices and the gut proteins that could have trapped ^{14}C -free carbon within the gut strings. We cannot exclude this hypothesis but it is not clear why this interaction would be visible only for early practices and not during our chemical treatments (see other strings analyzed in this study).

ii- making processes

Structural modifications occurred on early bowed instruments around 1800 (such as the replacement of the neck)(Boyden et al., 2001) and strings were subjected to higher and higher tensile strength. Thus, it is legitimate to wonder whether there were also changes in the making processes of gut strings in the early 19th c. as was the case for iron and steel piano strings during the same period (Durier et al., 2019). Although research on making processes in written sources is available (Dugot, 1983; Longhi, 2019; Houssay, 2004), material analyses aimed at deepening current knowledge on “gut string history” are currently limited to complete ^{14}C results.

As an example of preliminary material analyses, we observed that the lute strings MGD19 and MGD20 have opaque and dissociated strips whereas the Bernardel cello string MGD18 has more compact and almost translucent gut strips. This might be consistent with an observation reported by Houssay (2004) suggesting that pre-industrial gut strips were less tightly twisted than industrial gut strings (Chapter 1 – § 4.1). Besides, by comparing the gut string Baillot, c.1850 with the one from the Bernardel cello c.1896, we observed the same regularity in the

winding of the copper strings wrapped around the gut string, testifying to mechanization of the process. The introduction of steam machines in wire-drawing installations was estimated to have taken place c.1810-1820 (Durier et al., 2019).

Early gut strings were produced using artisanal techniques until the early 19th c., when industrial practices developed to respond to the main preoccupations of violin makers, i.e. regularity of the string diameter and pitch of the note. Since the Industrial Revolution, new chemical treatments in gut string making could have induced ¹⁴C contamination with old or young carbons which could explain our ¹⁴C results on the cello string MGD18 which gave an age older than 1898. Tsukamoto et al., 2020 reported the ageing of the ¹⁴C result on a gut string from a harp-lute c.1815 and suggested that carbon contamination could have occurred during the making process of 19th century gut strings. Patents from the 19th century were studied at the Musée de la musique showing the use of chemical substitutes for traditional products. For example, the use of sodium percarbonate (Na₂H₃CO) (Louvet 1873 n° 115 664), and olive oil for rubbing was replaced by paraffin oil dissolved in benzine and camphorated alcohol (Lutz 1901 n°314 103)⁵⁴. Currently, we are unable to determine whether chemical treatments during the making process could have induced ¹⁴C contamination on the cello string MGD18.

7. Discussion and summary

The discussion is divided into the following three parts: i- adaptation, pitfalls and recommendations for ¹⁴C dating methodology applied on Heritage objects, ii- interpretation of ¹⁴C dating results according to the nature of the Heritage materials studied, iii- discussion about new information collected on the Heritage objects studied.

The results from the previous in § 7.1 are summarized and reported in Table 35.

⁵⁴ Report, S. Vaiedelich, available at the Musée de la musique.

7.1. Summary of the ¹⁴C results

Table 35: Summary table of the results obtained – information on either the age of the object, its making or its use and restoration

object	sample	MGD	information on ...		
			... age	... manufacture	... use
Musical instruments					
Violin Pierre Saint-Paul, c. 1740	varnish	-	no ¹⁴ C dating [1]		traces of animal glue under UV light
Cello "Lafille"	varnish	MGD100	not conclusive [2]		
	varnish	MGD101	not conclusive [2]		
Cello Namy, 1773	varnish	MGD102	not conclusive [2]		
Baroque violin, 1993.1.1	varnish	MGD149	[1528 – 1550] (8.7%) [1634 – 1665] (79.9%) [1784 – 1794] (6.8%)	in agreement with the second half of the 18 th c.	
	varnish	MGD150	[1643 – 1684] (38.2%) [1736 – 1803] (52.8%) [1936 – ...] (4.4%)	in agreement with the second half of the 18 th c.	
Violin, Vaillant, 2015.8.1	varnish	MGD151	[1683 – 1735] (25.1%) [1802 – 1930] (70.3%)	in agreement with the early 19 th c.	
Furniture with European and Asian lacquers					
Cabinet Boulle, 18 th c., OA5468	lacquer	MGD123	[1445 – 1657] (95.4%) [3]	older than expected	likely contaminated by restoration products?
Chest of drawers Van Risen Burgh, 18 th c., OA11193	Chinese lacquer	MGD124	[1402 – 1529] (71.4%) [1542 – 1634] (24.1%) [3]	re-use of Asian lacquers	
	Japanese lacquer	MGD125	[1475 – 1640] (95.4%) [3]		
Horse-drawn carriages and sleds					
Snake and shell sled, CMV66, c.18 th c.	shell-shaped body	MGD134	[1439 – 1524] (69.0%)	older than expected	likely contaminated by restoration products?
		MGD135	[1571 – 1630] (26.4%)		
	coating of the gilded dashboard and runners	MGD136	[1642 – 1698] (24.1%) [1722 – 1814] (49.8%) [1836 – 1882] (6.2%)	- in agreement with the expected early 19 th c.	

			[1910 - ...] (15.4%)	- the shell body coats are dated prior to the gilded dashboard and runners coats	
Eagle sled, CMV57.006, c.18thc.	boiled oil	MGD133	not conclusive - ageing		restoration varnish of the 1960s in agreement with the "dossier d'oeuvre"
	pale blue coat	MGD132	not conclusive - ageing		contaminated by restoration products
	green coat	MGD131	not conclusive - ageing		
Dragon sled, CMV64, c.18thc.	red and gilded sample	MGD126	not conclusive - ageing		likely contaminated by restoration products
	pink preparation coat	MGD127	not conclusive - ageing		likely contaminated by restoration products
	gilded and yellowish coat	MGD128	not conclusive – ageing [4]		
	silver coat	MGD129	not conclusive		likely contaminated by restoration products
Golden Berlin carriage, CMV64.002, c.18thc.	metal leaves and binders	MGD137	not conclusive		likely contaminated by restoration products
	upper coats with shellac	MGD138	[1956 – 1957] (15.0%) [2011 – 2016] (80.4%)	linseed oil from 1960s	upper restoration varnish of the 1960s
	central white coats, metal leaves, oil binder		[1958 – 1959] (7.7%) [1986 – 1986] (0.6%) [1987 – 2001] (87.2%)	linseed oil from 1960s	diffusion of the restoration varnish of the 1960s
	lower preparation coats		not conclusive – ageing		
Sedan chair, CMV78, c.18thc.	brush hair	MGD139	[1958 – 1959] (7.2%) [1992 – 1992] (1.3%) [1993 – 2001] (86.9%)	restoration product	restoration of the 1960s
	run of brown varnish	MGD140	[1650 – 1695] (39.0%) [1726 – 1811] (42.5%) [1839 – 1842] (0.2%) [1873 – 1878] (0.3%) [1918 – 1954] (13.4%)	restoration product	restoration of the 1960s

Red and gold sled, TR1868, c.18thc.	Prussian blue coat	MGD147	not conclusive - ageing	contains geologically-derived Prussian blue	
	Upper red coats		not conclusive - ageing	ageing effect	likely contaminated by restoration products
Tortoise shell and silver leaf sled, TR88, c.18thc.	brown and blue decors	MGD142	no ¹⁴ C dating (inseparable layers)		original blue decor covered with a later brown decor
		MGD143			idem
	preparation coat (∃ white lead, Prussian blue)	MGD144	[1459 - 1683] (83.6) [1736 - 1803] (10.6) [1936 - ...] (1.2)	in agreement with the expected second half of 18 th c.	original blue preparation coats
Aventurine sled, TR41, c.18thc.	intermediate layers	MGD145	not conclusive - ageing	contains subfossil copal	original coats comprising oil and colophony covered with subfossil copal during the 19 th c.
Gut string of musical instruments					
Bernadel cello, 1896	gut string	MGD18	not conclusive - ageing	industrial fabrication process	- original gut strings (removed in 2017 at the public auction) - contaminated by rubbing products (e.g. paraffin, etc.)?
Battista Gabrielli violin, c. 1769	gut string	MGD32	[1808 – 1822] (12.3) [1831 – 1893] (83.2)	pre-industrial fabrication process (before 1900)	Frequent replacements of lute strings during playing period after 1769.
Lute Bunner, c. 1764	gut string	MGD19	[1764 - 1786] (73.3%) [1792 - 1801] (22.1%)	pre-industrial fabrication process (before 1900)	Frequent replacements of lute strings during playing period after 1764.
Lute Tielke, c. 1690	gut string	MGD20	[1773 – 1781] (84.8%) [1797 – 1804] (10.6%)	pre-industrial fabrication process (before 1900)	Frequent replacements of lute strings during playing period after c.1690.

[1] sampling using common chisels; in the remainder of the study, microchisels were used.

[2] did not benefit from protocol optimization for very small samples; not conclusive, likely because of the very small size that did not provide a sufficiently precise result

[3] age of the lacquer not of the object

[4] protocol error: the thermolysis cutoff was too high

7.2. ¹⁴C dating methodology on historical coatings

Here, we follow the different steps of the application of the protocols and their adaptations on early varnishes based on case studies with positive results followed by optimizations, pitfalls and limits of the method.

7.2.1. Adapting the sampling strategy

Documentation before sampling

During this PhD, the preliminary steps before selecting samples of interest for ¹⁴C dating on early varnishes began with the consultation of the “dossier d’oeuvre” for Heritage objects kept in museum collections. For objects from private collections, information was collected by contacting (previous) owners and/or professionals such as instrument makers, restorers, auctioneers, etc. (§ [Erreur ! Source du renvoi introuvable.](#)). Then, restorers examined the studied Heritage objects under UV light to identify successive layers of varnishes (e.g. cello, Namy, 1773 - Figure 45) and to avoid restored areas with probable carbon contaminating products; samples were taken preferentially on hidden parts. For example, samples were taken under bronze corners on the lacquered chest of drawers OA11193 (Table 22), on hardly accessible carved parts of the cello head “Lafille”, and on the backside of the soundboard of the violin 1993.1.1 expected to have been less subjected to restoration products. If contaminated areas could not be avoided, the nature of the restoration products was investigated to assess their impact on the original compounds (e.g. MGD140 - sedan chair CMV78 - Table 27). Our ¹⁴C dating results highlighted that it was extremely difficult to avoid restoration contaminations due to the even application of “protective” coatings in past decades such as on horse-drawn carriages kept at the Musée de Compiègne and the MRAH, Brussels, unless the restoration products did not penetrate the whole coating stratigraphy.

At this stage, some recommendations can be made to improve the sampling strategy:

- Select samples in hidden areas and less restored parts under UV light and based on previous restoration reports.
- Future restoration interventions should ideally preserve unrestored areas on the Heritage object as a testimony of its previous material state.
- Restoration interventions could be opportunities to take and store samples using suitable practices for ¹⁴C dating applications with a sufficient level of documentation such as the distribution of restoration products, the composition of the varnish stratigraphy, the initial location of the sample, etc.

Mechanical sampling

Although restorers developed extensive expertise in using solvents to remove varnish layers according to their organic composition, most of these products contain ¹⁴C contaminants. Thus, I tested mechanical sampling using a common chisel on a violin, Pierre Saint Paul, c.1740, private collection and an early violin bow n° inv. EO, Musée de la musique ([Appendix 4 – § 2](#)). As the varnish layers were not satisfactorily separated, I finally used microchisels to mechanically sample varnishes; this method has been validated as more appropriate ([see “sampling protocols”, § 3](#)).

During field missions, two strategies using microchisels were tested. On the one hand, varnish layers were sampled layer by layer under UV light and magnifying glasses (violin Vaillant 2015.8.1; Baroque violin 1993.1.1; red and gold sled TR1868; tortoise shell and silver leaf sled TR88; Aventurine sled TR41). On the other hand, complete or incomplete varnish stratigraphies were sampled using common chisels, then the layers were separated using microchisels under binocular microscope and UV light in the laboratory (Cabinet OA5468; chest of drawers OA11193; sleds CMV66, CMV57.006, CMV64, CMV64.002, CMV78).

However, better results were obtained *in situ* under binocular microscope and UV light and provided a good knowledge of the varnish stratigraphy (e.g. separation of the underlying wood Q5-1, lower black lacquer Q5-2, upper red lacquer Q5-3 on the Qiulai *qin* D.04224, Durier et al., 2021).

Based on our sampling experiments, some recommendations should be considered:

- Organic solvents are prohibited for sampling varnish layers to be dated using ¹⁴C. Mechanical microsampling is recommended.
- Our experience leads us to recommend sampling the varnish layer by layer *in situ* using microchisels under UV and binocular microscope, and provided a good knowledge of the varnish stratigraphy.

Clean conditions

The sampling conditions are decisive to ensure positive ¹⁴C dating results including carbon-free suitable tools and containers which are all baked at 450°C and covered with aluminum foil as routinely applied at the LSCE (see “sampling protocols”, § 3). As is routinely done for other samples, the varnish stratigraphies are wrapped in pre-baked aluminium foil and stored in a numbered plastic bag.

Some adaptations had to be made during this PhD to collect powdered varnish layers separated with micro-chisels. Glass is a suitable material for sample containers, but it can break and the sampled powder may stick to the inner walls by static electricity; thus, glass vials were chosen with an appropriate depth/diameter balance (glass shell vials 2 mL Øxh 12x32 mm). Before sampling, the glass tubes were pre-sealed with 3 aluminum foils (to form an aluminum cap) and pre-baked at 450°C. Finally, the tubes were covered with a plastic cap and placed in a suitable plastic box for greater stability.

Based on expertise at the LSCE and sampling experiments carried out during this PhD, here are some recommendations for sampling:

- Sample containers must be carbon-free such as glass tubes, aluminium capsules and aluminium foil. These carbon-free containers are then placed in plastic bags or boxes for safe transport.
- 2mL glass vials pre-baked at 450°C are suitable containers to collect powdered samples.

7.2.2. Adapting the chemical treatments

During this PhD, the chemical protocols were adapted to the nature of the subsamples from Heritage objects as described in the "specific chemical protocols" part of this chapter. We note that each sample is specific and that a unique protocol is not applicable to all of the material corpus.

A short overview is given in Table 36.

The sampled material is always in small amounts; our experience during this PhD showed that the recommended limit sample size sampling for ^{14}C dating is between 1 and 2 mg. A few 'tricks' were devised for pre-treatments before ^{14}C dating so as to ensure this. After an initial application of mechanical sampling using microchisels on two cellos, private collection (head of the cello carved by "Lafille" - MGD100 - Table 17 and the Namy Cello - MGD101 - Table 18), the amount of varnish was not sufficient and was also in a powdery state. Thus, the chemical protocol was adapted to limit material losses of varnish powder using narrow-bottomed tubes, rinsing and drying in a freeze-dryer (see "specific chemical treatments", § 4.1). Another example concerns the samples of varnish stratigraphies transported to the laboratory. They were carefully placed in aluminium capsules and observed under a binocular microscope in order to separate the varnish layers using microchisels. The subsamples remained in the aluminium capsules or they were placed in tin cups for AGE3 or EA-GIS without chemical treatments and/or placed in narrow bottomed tubes for chemical pre-treatments before ^{14}C dating.

During this PhD, we always attempted to use the minimum sample size in order to reduce the impact on the integrity of a Heritage object while being confident of obtaining conclusive ^{14}C measurements. As a result, we encountered difficulties in estimating the appropriate minimum sample mass needed for ^{14}C dating by scientists and the related varnish surface (as a scale for curators) which may depend on the studied object. It was decided to use a precision jewellery scale (G&G FC50) on field missions as the precision scales used at the LSCE (<1 mg) are not transportable. However, the jewellery scale only provides an estimation as its accuracy is ± 2 mg.

Moreover, the subsamples of early "bulk" varnishes are complex mixtures for which the carbon content is difficult to apprehend. Our first estimations by calculation did not match reality. It is necessary to take into account the weight of heterogeneous inorganic elements in early varnishes including heavy elements such as gold and silver, and the possibly weak proportion of organic binders (weak compared to inorganic pigments) for conclusive ^{14}C measurements. Therefore, CO_2 of several samples was extracted using the microline to have a reliable estimation of the carbon content (see "radiocarbon dating protocols" – § 4).

The ultimate aim is to design an abacus in order to anticipate the amount of carbon (μg) compared to the sampled mass or volume from the most common varnish ingredients. This could be as a form of a series of photos of different sized chips, each associated with an evaluation of the carbon mass in μgC . At this stage, knowledge is necessary about the material composition of early "bulk" varnishes, but also about the contemporaneity of carbons of the ingredients.

Table 36: overview of the lab protocols to apply on sub-samples of Heritage objects according to their nature and size

sample type	size	glass	chemistry	conversion into CO ₂	ECHOMICADAS introduction
wood	>600µgC	centrifugation tube	hot ABA	AGE3	solid source
	<600µgC	narrow-bottomed tube	hot ABA + freeze dryer is required + transfer into tin cup with LN2	EA-GIS	gas source
varnish	>600µgC	centrifugation tube	A + freeze dryer	AGE3	solid source
	<600µgC	narrow-bottomed tube	A + freeze dryer + transfer into quartz tube with LN2	micro-line	cracking GIS – gas source
pigment	>600µgC	narrow-bottomed tube	A + freeze dryer + transfer into quartz tube with LN2	micro-line	cracking-GIS – gas source
	<600µgC				
lead white	>600µgC	quartz tube	no chemistry – thermolysis 300°C	micro-line	"Gégé" - solid source
	<600µgC				cracking-GIS – gas source
gut string	>600µgC	vial	DCM/MeOH/Ac	AGE3	solid source
	<600µgC			EA-GIS	gas source

7.2.3. Adapting the material characterization strategy

¹⁴C dating combining material characterization

The first step consists in dividing the varnishes layer by layer based on observations under UV light using a binocular microscope and knowledge acquired on the composition of varnish stratigraphies through previous reports available in museums. As an example, for the chest of drawers OA11193, I was able to isolate varnish layers using the microchisels on the MGD125 sample as illustrated in Figure 61. The underlying white glue that yielded an unexpectedly old range of dates [BC 1500 - ...] was properly separated from the upper brown Japanese lacquers with the microchisels as shown by their uncontaminated ¹⁴C results (MGD125 - Table 22). At each step of the sampling including microscope observations, it is recommended to take a lot of pictures and micrographs to be able to ensure the identification of the sub-samples.

The strategy described above may not be sufficient to interpret ¹⁴C measurements and additional material characterization analyses might be required, depending on the time and budget of the project as well as the amount of sample and equipment available. As an example, the case study of the lacquer stratigraphy of the Chinese qin D.04224 included optical microscopy, VIS-UV-IR imagery, XRF and ATR-FTIR in a first step in order to complete historical knowledge on the composition of layers through early recipes (Durier et al., 2021). The pigments and binders initially expected did not supposedly have an impact on ¹⁴C dating. However, further analyses using SEM-EDS and Raman spectrometry revealed the unpredicted impact of residues from malachite despite pre-chemical treatments before ¹⁴C dating measurements.

Consequently, feedback can be obtained on the impact of some ingredients in early varnishes on ¹⁴C analyses. This will lead to better assessing the impact of pigments of geological or subfossil origin such as Prussian blue (TR1868, TR88 – Table 28, Table 29) and organic binders such as subfossil copals (TR41 – Table 30) as well as to better understanding how traces of restoration products such as acrylic distort the ¹⁴C dating results. The right protocol can then be better adapted to the material composition so as to eliminate or date lead white.

Material characterization analyses are time-consuming, thus the partnership with the Elinx project was a great opportunity since the organic and inorganic composition of the varnish stratigraphies had already been determined using respectively SEM-EDS and Py-GC-MS. This approach is the most recommended approach for ¹⁴C dating and was carried out for the Chinese *qin* except that the Py-GC-MS analyses were substituted by ATR-IRTF analyses due to the unavailability of the equipment.

During this PhD, one of the steps was to define which subsamples would be subjected to a material study and which would be subjected to ¹⁴C measurements. For most of the samples of varnish stratigraphies, it was decided not to divide them to perform further material characterization analyses since we were not confident that the sample size after separation of the layers would guarantee valid ¹⁴C results.

The final recommendations are:

- Take as many pictures and micrographs as possible to document the sampling.
- Develop the strategy by combining the following three disciplines: restoration/material characterization/¹⁴C dating.

- Before sampling for ^{14}C dating, perform physico-chemical analyses to characterize varnish microsamples using non-destructive analyses (ATR-IRTF, etc.) or micro-destructive analyses (GC-MS). Better results are expected using SEM-EDS and Py-GC-MS.

7.3. Effect of the nature of early varnishes on ^{14}C dating results

7.3.1. Natural organic binders

According to the state of the art on early varnishes ([Chapter 1 – § 3.1](#)), we expected to find linseed oil/colophony varnishes on lacquered pieces of furniture and horse-drawn carriages dated from the early 18th c. Indeed, the material corpus of this PhD mostly comprises early linseed oil/colophony varnishes (Cabinet OA5468; chest of drawers OA11193; red and gold sled TR1868; tortoise shell and silver leaf sled TR88; Aventurine sled TR41). Although the material analyses could not be performed on the sleds kept at the Musée de Compiègne, as was done during the ElinC project on sleds kept at the MRAH, Brussels, the presence of linseed oil/colophony coats was expected as well (CMV66, CMV57.006, CMV64, CMV64.002, CMV78).

Linseed oil/colophony varnishes

^{14}C dating measurements applied on early linseed oil/colophony varnishes are expected to provide contemporaneous results with the making period of the Heritage object as the historical study had shown that linseed oil or colophony was not subject to long-term storage practices. Violin makers might more likely have produced their own varnishes in batches stored for 1 or 4 years in glass bottles or new varnished pots to avoid dust contamination ([Chapter 1 – § 3.4](#)). Moreover, the ^{14}C dating measurements on lab-prepared linseed oil/colophony mixtures highlighted the dominant contribution of linseed oil after heating. The final carbon content measured for linseed oil represents 72 to 75% of the total carbon content whereas the initial proportions were 70:30 of linseed oil and colophony as reported in the literature on 17th c. Italian violin making (Echard, 2010) (Table 16). This confirms that linseed oil/colophony varnishes would provide ^{14}C results consistent with the period of their preparation and application as linseed oils were used fresh due to the alteration of their physico-chemical properties with ageing.

Gilding and silvering coats

The gilding and silvering coatings are also datable using ^{14}C dating due to their mixture composition. Oil/colophony mixture had been used on horse-drawn carriages since the early 18th c. (e.g. CMV66 - Table 23, [Chapter 1 – § 3.3.3](#)). Water-based techniques using animal glues could also be dated using ^{14}C dating.

Other natural resins

We were also confronted with other types of resins such as copal or shellac instead of colophony. Shellac varnishes were detected on most of the studied bowed instruments from the 18th c. (e.g. violins from Mirecourt) and are expected to be contemporaneous with the making period of the Heritage object. However, the socio-economic context might be worth investigating further to estimate the storage duration and transport of shellac from Asia to Europe. This historical approach could be extended to other natural resins such as sandarac used in early oil-based varnishes in the same way as it was conducted on colophony and turpentine.

Some organic binders derived from subfossil ingredients will lead to erroneous ^{14}C dating i.e. not contemporaneous with the making period of the varnishes. That is the case for subfossil copal resin, detected in the coating of the Aventurine sled (TR41) (Table 30).

- The ^{14}C dating of colophony-linseed oil varnishes gives results that are contemporaneous with the making period of the Heritage object since the storage period of varnishes is estimated to be short-term (1-4 years) (Chapter 1 – § 3.3.3).
- Natural varnishes containing shellac are expected to be contemporaneous with the application period. However, further studies are still needed on the early production and trade practices to better understand the storage duration.
- ^{14}C measurements of varnish containing (sub)fossil resins yields results that are not related to the date of the varnish application.

7.3.2. Pigments

In order to define the contemporaneity of carbons with the application period of early varnishes, it is essential to know the composition and mode of production of the pigment over time. During this PhD, we were faced with dark or light blues (CMV57.006 - Table 24, TR1868 - Table 28, TR88 - Table 29), reds (CMV64 - Table 25, TR1868 - Table 28, D.04224 - Durier et al. 2021), greens (CMV57.006 - Table 24), yellows (CMV66 - Table 23), and black (TR41 - Figure 96; D.04224 - Durier et al., 2021).

Despite chemical pre-treatments before ^{14}C dating, we highlighted that some pigments contaminated our ^{14}C results, such as **malachite** which is a copper carbonate $\text{Cu}_2\text{CO}_3(\text{OH})_2$ of geological origin. After a classical A chemical treatment, a residue with 30-20% of geological carbons from the malachite mineral structure induced an ageing of the ^{14}C measurement on a sample of the lower black lacquer from a Chinese *qin* D.2442 (Durier et al., 2021).

There is also an issue regarding the effect of **Prussian blue** on ^{14}C dating. This pigment was used since the early 18th c. and its recipes changed according to the historical period (Chapter 2 – § 4.2.2.2). Thus, the geological or biological provenance of carbons in cyanides is not clearly determined based on literature research. As the triple bonds between carbon and nitrogen are resistant to a classical A chemical treatment, we feared a possible ageing of the blue binders if these carbons were of geological origin. This was observed on a blue coat of the sled TR1868 (Table 28), but not for a blue coat of the sled TR88 (Table 29).

This pitfall may ultimately be a blessing in disguise. ^{14}C dating could indeed be used to detect the presence of pigments of geological or (sub)fossil origins that were not initially identified using previous material analyses. For example, **bituminous substances** were used as black pigment on horse-drawn carriages during the 19th c and they are hard to distinguish from other types black carbon by infrared spectroscopy (Durier et al., 2022). The ageing observed in ^{14}C dating is thus a clue to their identification.

Fortunately, the pigments were not all of (sub)fossil or geological origin. During this PhD, we encountered organic and inorganic pigments which did not induce ^{14}C contamination. They were either free of fossil carbon or a classical A chemical treatment was sufficient to dissolve carbons of geological origin. Some pigments do not contain carbon at all. This is the case of **vermillion** or **cinnabar** (HgS), **ochres**, **iron oxides**, **lead-tin yellow** (Pb_2SnO_4), **ultramarine** ($\text{Al}_6\text{Na}_8\text{O}_{24}\text{S}_3\text{Si}_6$), **smalt** (potassium cobalt silicate) and other cobalt blue pigments (Al_2CoO_4) such as **cerulean** (SnO_3Co), **minium** (lead (II, IV) tetroxide), **gold**, **silver**, etc. Other pigments such as **carmin** lacquer (e.g. TR1868 - Figure 87) or **black bone** contain carbons of biological origin

which are contemporaneous with the making period. The copper carbonates in **verdigris pigment** ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) contain carbon contemporaneous with the making period as it derives from the oxidizing agent (vinegar, acetic acid, wine) involved in the making process.

- ^{14}C measurements can inform on the mode of production of some pigments (e.g. Prussian blue) or on the geological or (sub)fossil origin of the pigment ingredients (e.g. malachite, bitumen).
- Most of the pigments that we encountered did not imply ^{14}C dating contamination.

7.3.3. Chalk and lead white

The preparation coats on early horse-drawn carriages are often made of lead white (e.g. TR1868 - Figure 87, TR88 - Figure 92) and/or chalk (e.g. TR41 - Figure 96) mixed with a small amount of organic binder. By using the correct thermal decomposition protocol, *i.e.* the one recommending a cut-off at 300°C (Messenger, 2020) and not 400°C (Beck et al., 2019), it is possible to separate carbonates with carbons of organic origin and of geological origin to obtain the date of the lead white preparation. This was the case for the tortoise shell sled (TR88 - Table 29) but unfortunately not for the dragon sled (CMV64 - Table 25) for which the wrong protocol had been applied.

Lead white could be used as a drier for linseed oil/colophony varnishes in violin making and horse-drawn coatings. As **calcium carbonate** (and also **magnesium carbonate**) from chalk and carbonates from lead white are very reactive in the presence of a strong acid such as HCl, it was sufficient to apply an acid treatment to eliminate the geological carbon carbonates introduced during the production of lead white.

The treatments described below for lead white could be extended to other pigments to separate carbons from different crystal cohesions, such as freshly precipitated or biological carbonate from geological carbonate.

- To eliminate both geological and freshly precipitated carbonates from the lead white added in oil-based varnishes, acid treatment (HCl) is sufficient.
- The date of manufacture of lead white-based preparation coats is obtained by ^{14}C analysis of the CO_2 evolved by thermal decomposition under 300°C .
- These strategies could be extended to other pigments comparable to lead white.

7.3.4. Restoration

Unfortunately, we often encountered restorations that had a high impact on the ^{14}C measurements performed during this PhD. These restorations may involve the use of xylophage, acrylic binders, etc. Carbon contamination by restoration products such as linseed oil from the 1960s ($F^{14}\text{C} \gg 1$) and petroleum-based products which contain dead carbons ($F^{14}\text{C}=0$) can modernize or age ^{14}C results on samples (Table 37). Despite our best efforts to select unrestored areas, it proved difficult to avoid traces of restoration products when they had been applied evenly on the surface (as if for “protective” purposes). Past restoration interventions are not always visible or documented.

Table 37. Impact of some common restoration products encountered during this PhD on ¹⁴C dating measurements.

Ageing restoration products	Modernized restoration products
<p><u>Products older than the restoration period:</u></p> <p>Petroleum-based solvents such as:</p> <p>White spirit</p> <p>Xylamon (C₂₂H₁₈Cl₂FNO₃, C₁₂H₁₁Cl₂N₃O₂)</p> <p>Paraffin</p> <p>Acrylic binders (acrylic resin Paraloid B 72, ethyl acetate; Plextol B 500 B 360)</p> <p>Polyester-styrene binders</p> <p>Ketone binders</p> <p>Synthetic adhesives</p>	<p><u>Products dating from the restoration period:</u></p> <p>Natural oils (linseed oil, etc.)</p> <p>Natural resins (sandarac, dammar, shellac, benzoin, etc.)</p> <p>Natural wax (beeswax)</p> <p>Animal glues</p> <p><u>Products younger than the restoration period:</u></p> <p>Fish glues</p>

When products used to re-varnish an object have a ¹⁴C content related to the application period (i.e. in equilibrium with the ¹⁴C atmospheric content), this implies the addition of a layer that is enriched in ¹⁴C compared to the original varnish layer, even if the same ingredients are/were used. The additional layer cannot provide any information about the object manufacture but informs on the restoration phase and thus on the use(s) of the Heritage object. We obtained this kind of information for the Golden Berlin carriage (CMV64.002 – Table 26) and the Sedan chair (CMV78 - Table 27). The results on the Berlin carriage and the Sedan chair showed that the linseed oil varnishes from the 1960s were applied during a museum intervention. However, our results showed that the linseed oil from the 1960s had not been applied on the snake and shell sled during the same general museum intervention at the Musée de Compiègne (CMV66 - Table 20).

When the ¹⁴C content of restoration materials is/was not related to the application period, ¹⁴C measurement may inform on the nature of the products but not on its period of application nor on the period at which the object was made. As an example, the upper layer on the eagle sled yielded a ¹⁴C dating result consistent with the presence of a petroleum-based varnish (e.g. linseed oil diluted in white spirit) (CMV57.006 - Table 24).

During this PhD, attempts were made to separate the uppermost layers using microchisels in order to remove the dusty surface layer or the “protective” film and thus to reach the “uncontaminated” lower layers. For example, the top coats of paraffin or beeswax applied in the 1980s on the sleds kept at the MRAH, Brussels, were mechanically removed before the sampling (e.g. gold and red sled - TR1868 - Table 28). This strategy also allowed for relevant results by removing the thin organic bronze surface patina (from a likely later restoration) that covered the original oil gilding layer on the snake and shell sled (CMV66 - MGD136 - Table 20): [1642–1698], [1722–1814], [1836–1882], [1910– ...]. This strategy also provided positive ¹⁴C dating results in line with the historical record on a red lacquer sampled after removing the non-original dusty surface film on a Chinese *qin* D.04224 (Durier et al., 2021).

Restoration interventions may also have involved the application of underlying glues to consolidate varnish chips. In the case of the chest of drawers OA11193, I was able to isolate the underlying white glue from the upper lacquer layers. Its origin as an original or a restoration

glue has not been defined. The amount of carbon (4 µgC) was too low for ¹⁴C analysis (OA11193 - MGD125 - Table 22).

Some restoration treatments can involve the addition of upper layers on a varnish stratigraphy without contaminating the lower layers. But the removal of the most recent restoration materials using microchisels may not be sufficient in the case of impregnation and diffusion of the products. This is what we observed for the Eagle sled (CMV57.006 - Table 24) and the Dragon sled (CMV64 - Table 25). Our results informed us on the nature of the restoration products, most likely containing petroleum-derived compounds, but also distorted the ¹⁴C measurement of the underlying original layers. For example, the diffusion of linseed oil applied in the 1960s is visible on the intermediate layers from our ¹⁴C results on the Golden Berlin carriage.

- Restoration products can distort the ¹⁴C dating by making the age of the original varnish layer younger or older.
- Restoration products using natural binders inform on the restoration period.
- ¹⁴C dating on petroleum-derived restoration products gives information on their nature, but not on the application period.
- Restoration products may also have an impact on the intermediate layers by diffusion.

7.4. Information collected on the studied Heritage objects

All the results are shown in Table 35 and are discussed in the previous part. We here sum up the knowledge we were able to extract from the ¹⁴C investigation.

7.4.1. Musical instruments

Unfortunately, we were not able to provide conclusive information on the **cello head carved by “Lafille”** nor on the **cello Namy**, 18th c., Paris, private collection. The ¹⁴C dating measurements were not precise enough to produce narrow intervals of calibrated dates. The sampling occurred at the very beginning of the study and both the amount of material that was collected was small and the chemistry protocol in the lab had not yet been optimized for such small amounts of material and powdery samples. With the hindsight we have today, we are confident that we could have obtained conclusive results.

The violins of the Mirecourt museum benefited from the optimization of the procedures. Two of them were sampled to discuss their making period in the early or late 18th c. or early 19th c. in comparison with historical documentation, stylistic comparison and dendrochronological results. The **Baroque violin 1993.1.1** was firstly dated between 1699-1710 according to a stylistic study; however, our ¹⁴C dating tends to confirm the dendrochronological results (Ratcliff, unpublished), i.e. the [1736 – 1803] or [1784 – 1794] intervals.

¹⁴C dating on the **Vaillant violin 2015.8.1** (late 18th c. - early 19th c.) on a varnish sample of the soundboard yielded a compatible interval [1802 – 1930]. This part of the violin is highly exposed to maintenance solvents ([Chapter 1 – § 3.2.2](#)). A priori, pigments (earths, ochres, vermilion, etc.) in violin making are not expected to affect ¹⁴C dating.

¹⁴C dating results on the upper red lacquer of the **Chinese qin D.04224** provided calibrated dates relevant with the making period since the ingredients are not contaminants for ¹⁴C dating. The intervals yielded were compared with Chinese inscriptions and material characterization,

making it possible to determine the interval [1659–1699] as the most likely making period. ¹⁴C dating results on the lower black lacquer revealed the presence of malachite as residual geological carbonates resisted routine acid pretreatment of the sample (Durier et al., 2021).

7.4.2. Furniture at the Musée du Louvre

The two pieces of furniture show the European taste for Asian lacquers and their imitations since the end of the 17th c. and which developed during the 18th c. The lacquer of the **Cabinet Boulle OA5468** is dated [1445-1657] (Table 21) and the Japanese and Chinese lacquers of the **chest of drawers Van Risen Burgh OA11193**, respectively, [1395AD – 1475] and [1475 – 1640] (Table 22). The chest of drawers is especially representative of an early 18th c. practice, i.e. the reuse of Asian lacquer associated or not with European lacquer. The French merchant Thomas-Joachim Hébert (1687–1773) is known to have sold that kind of furniture. Our ¹⁴C results highlighted the early practices of reuse of Asian lacquers and wooden panels that were much older than the period at which the studied Heritage objects were made.

7.4.3. Sleds, carriages and chair

It makes sense to date the original coats of early horse-drawn carriages in order to determine their making period rather than to date the wooden parts. However, we were confronted with the impact of various pigments, binders and restoration products that mainly provided us with information about the making processes and the use(s) of the objects through time, rather than about the making period.

The ¹⁴C dating on the coats of the **snake and shell sled CMV66** validated the initial assumption that the undergear was from a latter making period. The results on the gilded dashboard yielded the [1836–1882] interval (Table 23), which is consistent with the expected making period of the undergear in the early 19th c. However, the dating of the marbled brown and yellow coats on the shell-shaped body is older than expected, highlighting not only the absence of a “protective” coat of linseed oil applied in the 1960s as for other carriages but also the use of petroleum-derived restoration products since the pigments used, such as ochre, are not expected to impact ¹⁴C measurements.

The ¹⁴C dating of the upper varnish which was expected to be dated from the 1960s on the **dragon sled CMV57.006** provided older dates that are consistent with the use of a petroleum-based varnish and other products such as xylamon and acrylic glues (Table 24). Unfortunately, the product was evenly applied on the green and blue coats of the undergear and the body, impacting even the lower layers.

The ¹⁴C dating on a complete stratigraphy on the runners of the **dragon sled CMV64** showed that an upper petroleum-based product was also applied evenly, most likely in the 1960s, leading to a strong ageing of each intermediate layer with a lower contamination on the preparation layers (Table 25). The ageing was also noted on a silver coat of the body of the sled. We argue that acrylic binders might have been used here.

The ¹⁴C dating results showed that the **golden Berlin carriage CMV64.002** and the **sedan chair CMV.78** were heavily covered with linseed oil from the 1960s. Unfortunately, this product caused strong ¹⁴C contamination from the bomb peak, going as deep as the intermediate layers, providing the dates: [1958 – 1959] (Table 27). The preparation layer of the golden Berlin carriage that should have been less affected contained mostly geological carbonates, which means chalk rather than lead white, according to our ¹⁴C dating measurements.

The ^{14}C dating of the upper red coats on the **red and gold sled TR1868** provided a date interval older than the expected making period in the early 18th c. according to stylistic comparison. This result could be due to the impact of the upper wax surface applied in the 1980s despite a careful scatter of this “protective” layer before sampling. The ^{14}C dating of the Prussian blue for the red and gold sled TR1868 and for the **tortoise shell and silver leaf sled TR88** respectively provided a range of dates older than the expected making period (Table 28) and a range of dates in agreement with the expected period within the second half of the 18th c. [1736 - 1803] (Table 29). We suggest that different making processes were used for Prussian blue and that this might be responsible for these discrepant results.

The ^{14}C dating on the green coats of the **Aventurine sled TR41**, dated from the second half of the 18th c. according to stylistic comparison provided a range of dates that was older than expected (Table 30). The presence of Prussian blue could be responsible. However, the carbon content of the sample is high and another source of contamination in the organic binder is suspected. We argue that the use of subfossil copal could have contaminated the ^{14}C content of the coats (Chapter 1 – § 3.5).

Finally, ^{14}C dating applied on horse-drawn carriages could provide interpretable results on the making periods and making processes depending on the restoration practices. For example, horse-drawn carriages could have been restored in a similar way to easel paintings by removing the varnish layers using solvents that can no longer be dated. Restoration that was carried out using products that are strong markers of the ^{14}C content (petroleum derivatives, $F^{14}\text{C}=0$ or from the bomb peak, $F^{14}\text{C} \gg 1$) could also strongly contaminate the lower layers by diffusion.

7.4.4. Gut strings

We analyzed four gut strings taken from a cello, a violin and two lutes of known origin and age. For both lutes, we were able to determine an end of musical use before the 19th c. using ^{14}C dating since the strings are dated from the second half of the 18th c.: [1764 – 1786] and [1792 – 1801] for the **lute Bunner** (Table 32) and [1773 -1781] and [1797 – 1804] for the **lute Tielke** (Table 31). Preliminary material observations provide clues to the pre-industrial making of these gut strings.

The ^{14}C dating of the gut strings of the **Battista Gabrielli violin** covering the 19th c. ([1808-1822] and [1831–1893] – Table 33) indicates a more recent (musical) use of the strings on the violin. According to the instrument making expertise, they may have been replaced after later visible interventions on the violin.

Finally, the ^{14}C dating of the **cello Bernardel** does not inform on the year of the string making but on its making process. Preliminary material observations provide clues about the industrial fabrication of the studied gut string. However, the calibration of the ^{14}C analysis (Table 34) is older than the date of manufacture of the instrument (1896) which is highly improbable. We argue for the introduction of older carbons at the time when the string was made, for example using petroleum derivatives including chemical treatments developed during the Industrial Revolution. The fabrication process for gut strings from this period may have undergone major changes, as was the case for steel piano strings, in order to increase the mechanical resistance to the higher tensions applied to strings during musical performances in the 19th c.

8. Conclusion

^{14}C dating requires to be used in tandem with restoration, material science and museum expertise.

- The mechanical sampling was adapted based on a survey among restorers.
- Obviously, the more that is known about the chemical composition of the varnish layers, the more the protocols used before ^{14}C dating can be adapted beforehand and the more reasonable the interpretation of the results will be. However, the effect of pigments such as Prussian blue on ^{14}C measurements is still not well determined. The same holds for the chemical interactions between pigments and the organic binders which can induce problems during thermolysis or chemical treatments for carbon extraction. The methodologies and development are still in progress such as the case of lead white and chalk mixtures (Hendriks et al., 2016, 2020).
- Museum information provides *termini ante* and *post quem* for the making period or clues about the material history of the object.

The level of documentation in each field regarding the characterization of materials, the origin and material history of the object, and the historical context of manufacture provide clues for ^{14}C dating expertise. In the same way, ^{14}C measurements contribute a new level of information, providing fresh clues for further research in other fields such as the study case of the Chinese zither or qin, no. inv. D.04224.

CHAPTER 4. Contribution of strontium isotopic geochemistry to the determination of the geographical origins of natural varnishes – feasibility study

1. Introduction

One of the objectives of this thesis was to investigate the possibilities offered by geochemistry for tracing the origins of materials used in musical instruments. The results obtained with organic geochemistry were given in chapter 2 and Appendix 1. This chapter describes the results obtained with strontium isotope geochemistry and evaluates its potential. We investigated the feasibility of the approach for the components of varnishes (colophony and linseed oil) and the original natural elements (pine resins, soil). The aim was to assess the applicability of the methodology to linseed-oil varnishes with a view to adding a tool to the study of musical instruments from the 17th and 18th centuries. This investigation was carried out using the LSCE's facilities for sample preparation, its clean-lab for chemical preparation, and the MC-ICPMS mass spectrometer (NEPTUNE PlusTM by Thermo ScientificTM) operated at LSCE by the GeoTrAc group for the precise measurement of radiogenic isotopic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

The chapter is in two parts. First, a part that unfolds the methodological problems that we had to circumvent and then a presentation and interpretation of the reliable results. The outline of the "methodological development" part will be as follows: description of the general principles and postulates (part 2), the expected problems (part 3), the initial experimental protocols in four steps (part 4) and the adaptations set up to counteract these difficulties (part 5), and the results based on these improved experimental designs (part 6). Then comes a table summarizing all the reliable measurements and their interpretation in the discussion (part 7).

2. Methods – general principles

2.1. Strontium and $^{87}\text{Sr}/^{86}\text{Sr}$ distribution within the geological realm

Strontium is an alkaline earth metal, with chemical properties close to those of calcium; it is found naturally in rocks, water and the atmosphere as a trace element. The distribution of its content in soils is available through geochemical atlases based on global geological surveys. Geochemical databases and maps are accessible for four continents: North and South America, Europe, East Asia, and Australia (Caritat et al., 2018; Blanchet, 2019). However, data access varies from one country to another and the data were not collected uniformly at the same level of detail. Each country or region uses different sampling strategies and field protocols depending on the specific scientific issues investigated. For example, detailed Sr content

mapping is available for France or the Middle East (Gregoricka, 2013; Willmes et al., 2014; Hoogewerff et al., 2019)(Figure 107a), whereas only unpublished surveys exist for other areas.

The Sr element comprises four natural stable isotopes ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr . ^{88}Sr is the most abundant Sr isotope in rocks. The radiogenic isotope ^{87}Sr is produced by the radioactive decay of ^{87}Rb . The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio then increases with time, with the age of the rock, and is specific to the local geological bedrocks according to their initial formation, their mineral composition and age (Faure and Powell, 1972; Faure, 1986). The modelled maps of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio called isoscapes (isotopic landscapes) are being increasingly developed and include ever more accurate spatio-temporal Sr variations (Bataille et al., 2020). The geology of Europe in general, and France in particular, is varied and complex. The shallow substratum and derived sediments are of a very wide range of age and kind of rock, leading to a highly different isotopic signature in strontium. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in Europe ranges from 0.700 to 0.760 (Hoogewerff et al., 2019). The same magnitude of geological diversity and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is also found in France (0.704-0.722) with clear regional trends (www.irhumdatabase.com, Willmes et al., 2018). The geological pattern is sufficiently diversified in Europe and France to discriminate between pine growing areas, coasts, fluvial valleys or mountains, such as the Landes and the Alpes in France (Willmes et al., 2018; Hoogewerff et al., 2019) (Figure 107b).

Besides the local Sr, the isotopes of which are directly associated to the geology, allochthonous Sr can also be found. The sources of non-local Sr may be natural or anthropic environmental contamination. Natural contamination includes allochthonous, sediment inputs by erosion, dry or wet atmospheric deposits such as, for example, long-range transport of Saharan particles, sea spray or rainwater (Bentley, 2006; Kamenov et al., 2009; Evans et al., 2010; Frei and Frei, 2013; Willmes et al., 2014; Price et al., 2002; Kochergina et al., 2021). Particular attention has been paid to natural contamination by local erosion with particles from younger or older bedrocks (Åberg et al., 1989). Natural geochemical cycles are also affected by anthropic activities through organic and mineral matter released into the air, water and soil by pharmaceuticals, agricultural fertilisers, fossil fuel, mining and quarrying deposits, etc. (Bentley et al., 2004; Kamenov et al., 2009; Maurer et al., 2012). Natural and human contamination may locally slightly impact the spatial distribution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio through time, for example in soils or in deposit or sediment materials, due to past and present land or soil uses or historical agricultural activities (Aguzzoni et al., 2018). In addition, a few specific areas are under the direct influence of possible natural contamination (e.g. coastal areas) and may be further impacted. This effect has to be assessed on a case-by-case basis by each specific field study. However, in our study and in most forest/pine locations, these types of contamination remain at the trace level and do not disturb the original local signature in strontium isotopes to any significant extent.

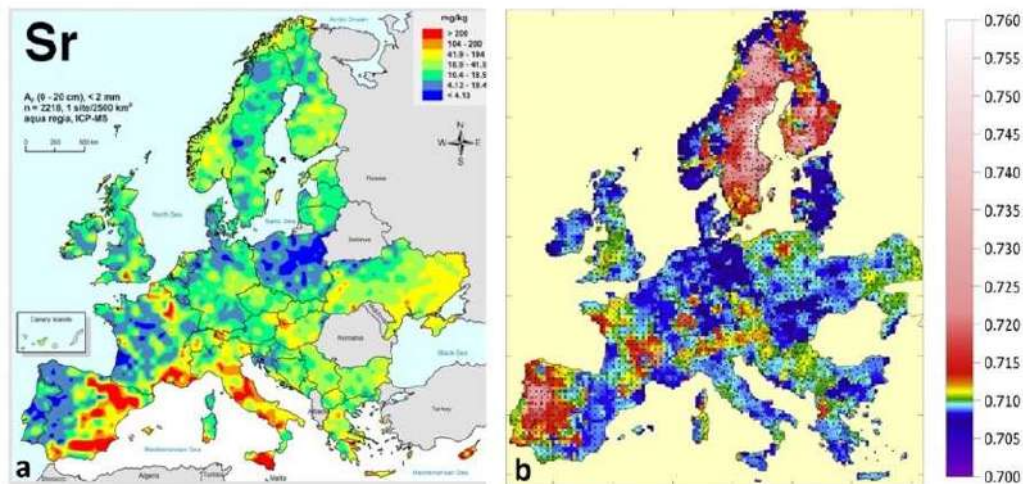


Figure 107. a) Sr geochemical map from the GEMAS project and b) $^{87}\text{Sr}/^{86}\text{Sr}$ modelled map in Europe (modified from Hoogewerff et al., 2019).

- The geochemical distribution of Sr isotopes is sufficiently diversified in Europe and France to discriminate between geological terroirs (Figure 107).

2.2. $^{87}\text{Sr}/^{86}\text{Sr}$ distribution in the Sr cycle, from mineral to plant and processed products

Owing to the weathering of the underlying local geology, strontium spreads into ecosystems of the terroir through soil particles, groundwater, then plants, herbivores, and finally omnivores and carnivores (Dasch, 1969; Hurst and Davis, 1981; Price, 1994; Gregoricka, 2013) (Figure 108).

Based on the conservative postulate that Sr isotopic ratios might not be naturally submitted to fractionation due to the small relative mass differences between strontium isotopes (only 1 atomic mass unit from 86) (Faure, 1986), the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio could be used as a radiogenic signature of natural materials from distinct geological terroirs. Over the past few decades, geochemical studies have successfully traced geographical provenances assuming that the weathering of local bedrocks is the main contributor to the strontium environmental cycle (Bentley, 2006; Crowley et al., 2017). Since the radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the ecosystem is assumed to reflect the isotopic imprint in the underlying local geology, geological and geochemical maps from continental to regional scales are used as references for archaeological or current provenance studies (Knudson et al., 2014; Snoeck et al., 2020).

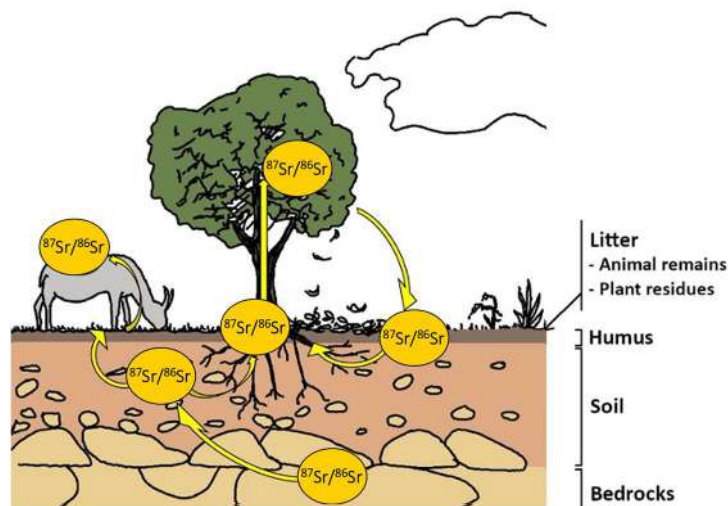


Figure 108. Sr cycle in the biosphere

Strontium isotope analyses are commonly applied in the field of archaeology, archaeozoology, population or individual migration studies, forensic science studies, illegal mislabelling and fraud control in food and goods, such as the ivory trade (van der Merwe et al., 1990; Rauch et al., 2007; Hoogewerff, 2010; Kars and Davies, 2012; Slovak and Paytan, 2012; Wang et al., 2016; Liu et al., 2019; Ryan et al., 2021). Sr isotope analyses are used, for example, in wood provenance studies to trace the origin of shipwreck timbers or the trade of exotic wood (Miller et al., 2012; Hajj et al., 2017). The isotopic approach opens up new perspectives for examining wooden instruments implementing dendro-provenance studies (Bernabei, 2020).

However, a caveat has recently been expressed about the conservatism assumption. Locally, the heterogeneity of the soil and the range of $^{87}\text{Sr}/^{86}\text{Sr}$ values of the material/particles composing it are not always well-constrained. And it is possible that not all the strontium is used by living organisms. This may eventually result in an isotopic fractionation between the total strontium measurable in rocks and the bioavailable part found in living organisms. The radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured in plants correlates better with the strontium ratio contained in the soil bioavailable fraction than with that of the total soil (Sillen et al., 1998; Song et al., 2014; Vinciguerra et al., 2016). During the process of differential leaching of minerals or organic matter composing the soil, marked by heterogeneous isotopic compositions in Sr, some minerals such as carbonates can be more soluble, releasing Sr more easily; in this case, the Sr is more labile than in minerals such as silicates. Then, the minerals are further combined with organic matter to form the clay-humic complex, a reservoir of nutrients available for plant roots which can also be a reservoir in Sr. As a result, if the bioavailable Sr fraction comes mainly from the carbonate fraction in a soil marked by a lower Sr isotopic ratio, then the plants will incorporate Sr with values lower than the Sr isotopic values of the total soil or of the silicate fraction of soils (Poszwa et al., 2004; van der Heijden et al., 2017). Numerous isoscapes such as the values in the IRHUM database (www.irhumdatabase.com) therefore consider the bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Evans et al., 2010; Willmes et al., 2018; Hoogewerff et al., 2019). The distribution of the local range of strontium isotope ratios is usually completed by empirical references using $^{87}\text{Sr}/^{86}\text{Sr}$ measurements on plants or animals that lived locally (Bentley 2004, Ryan 2021). Nevertheless, even if pH and soil composition are parameters that influence the absorption of Sr and its potential isotopic fractionation by plants, Sr accessible for biological assimilation is mainly derived from the weathering of bedrocks (Guibourdenche, 2018).

In the literature, isotopic provenance studies rely on the absence of fractionation in the soil-plant system. Vinciguerra et al. (2016) reported the conservation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the soil-plant-fruit system, and even in the soil-vine-grapes-wine system. The absence of fractionation in a manufactured product such as wine is due to insignificant mass differences of the strontium isotopes, which are not affected by biochemical reactions (Guibourdenche 2018). Owing to the conservation postulate, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been successfully used on Asian lacquers to trace the provenance of tree resin in drying oil/lacquer sap coatings (Lu et al., 2015; Nakagawa et al., 2019). Honda et al. (2016) reported that the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of Japanese lacquers is lower than that of Chinese and Korean lacquers, a finding that was used in order to reveal early trade routes between China, Korea and the different regions of Japan.

- Apart from a tiny isotopic fractionation associated to strontium bioavailability, the isotopic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of any biological organism, or manufactured product that derives from it, can be powerfully used to trace the original geological terroir from which it originated (Figure 108). When available, isoscapes (IRHUM database) of bioavailable strontium should be preferred as a reference for the origin of biological (derived-) products.

2.3. Research perspective: the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in linseed oil/colophony varnishes

Whilst convinced by the studies that have already verified the postulate of conservation in different cases, we also verified in this research project that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio remained constant throughout the transformation chain of interest: i- for the soil-pine-resin system, and ii- for colophony as a transformed product of pine resin, i.e. a residue of resin distillation, with potential contamination during the process or the recipients used. Consequently, we carried out experiments to verify that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio remained constant from soils to natural resins and even after harvesting and distillation. This verification was done on current materials and on historical materials.

The provenance of early colophony might be discriminated by cross-linking $^{87}\text{Sr}/^{86}\text{Sr}$ isoscapes with knowledge of the historical centres of pine products (Gascogne, Provence, etc.) and the distribution of the early centres of violin making: Cremona (Pô plain, Italy), Mirecourt (Vosges, France), Absam (Austria), the Mittenwald school (Bavaria, Germany), the Füssen school (Bavaria, Germany), the Saxony school (Markneukirchen, Germany), Lyon (Rhône, France), etc.

A major production of flax for the textile trade and cold pressed linseed oil for painting materials was historically implanted in northern Europe, from northern France to Belgium and the Netherlands with a constant Sr isotopic signature due to the underlying Quaternary sediments (Hoogewerff et al., 2019).

- The verification of the general principles of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio conservation was part of this research. It confirms its use as a geochemical marker to study the geographical provenance of European colophony and natural linseed oil/resin varnishes.

2.4. State of the art of the isotopic measurement of Sr at the LSCE

Strontium isotope analyses of natural or archaeological materials at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE, France) are performed on a Thermo Scientific™ Neptune Plus Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS). The analytical method for measurement of Sr isotopes using MC-ICPMS at LSCE was

first published by Palmiotto et al. (2013) and recently revised (Ryan et al., 2021). Usually, the protocol is adapted for various natural archives such as seawater, freshwater, solutions, carbonates (corals, speleothems), hydroxyapatite (bone, tooth enamel), soils, actual or ancient plant material, etc.

"Mineralisation procedure" (digestion, combustion...) & chemical separation of strontium

Briefly, the Sr in the sample needs to be extracted and purified, generally in a clean lab, before its isotopic measurement. Consequently, digestion and ion chromatographic procedures are applied. Generally, the selected sample is mechanically cleaned and weighed in Teflon beakers or porcelain crucibles with lids. Chemical cleaning steps (water, acids, etc.) have to be applied depending on the matrix analysed. Then, the sample is dissolved (beakers) or ashed in a muffle furnace at 550 °C (crucibles) using appropriate thermal protocols. Ashes (i.e. plants), are then dissolved in a 1:1 mixture of 8 M HNO₃ and 30% H₂O₂ for 24 h at 100 °C for 18 h in Teflon, after which the solutions are dried on a hotplate at 80 °C. Samples are taken up in a 3 M HNO₃ solution and loaded onto cation exchange columns charged with Sr-Spec (Eichrome Inc.) resin which has been intensively pre-cleaned. Finally, strontium is eluted in 2.5 mL ultrapure Milli-Q. The purified strontium fractions are adjusted to a strontium concentration of 20 ppb (µg/l) by dilution with 0.5 N HNO₃. To adjust concentrations, an aliquot of each purified-Sr solution is systematically pre-analysed using the LSCE's Thermo Scientific™ Inductively Coupled Plasma Quadrupole Mass Spectrometer (ICP-QMS) Xseries-II.

Measurement of Sr isotopes using MC-ICPMS

Both the prepared 20-ppb sample and standard solutions are introduced in the mass spectrometer MC-ICPMS. Notably, an APEX Omega is now currently used as the desolvating system with a 100 µl/min nebulizer. The sensitivity for a 20 ppb Sr solution is around 30 V on the ⁸⁸Sr peak and the blank contribution (0.5 N HNO₃) is around 0.05 V. The samples and standards are analysed in static multi-collection mode in a single block of 90 cycles with an integration time of 4 s per cycle. No isobaric correction is required for Ca dimers/argides and only minor corrections for ⁸⁷Rb to ⁸⁷Sr are considered. A correction is also applied for krypton (Kr) isobaric interferences (⁸⁶Kr on ⁸⁶Sr). In general, the chemical purification of Sr renders the effects of doubly charged Rare Earth Elements (REE) on the Sr isotope masses negligible due to the very low absolute REE abundances. Nevertheless, the REE effects, especially on the ⁸²Kr/⁸³Kr ratio, are systematically checked. The reproducibility of the ⁸⁷Sr/⁸⁶Sr measurements is evaluated through replicate analyses of the NBS 987 standard. Isotopic ratios are corrected using a standard-sample bracketing method and normalized to the NBS 987 standard value of 0.710245 and the external reproducibility of around 15-20 ppm (2σ) is commonly determined with uncertainties on the fifth/sixth digits. For each sample, the ⁸⁷Sr/⁸⁶Sr value is reported with a 2σ uncertainty, taking into account the standard reproducibility and the standard measurement error of each sample. It can be noted that this protocol is routinely applied at the LSCE for natural materials that are sufficiently rich in strontium (the blank contribution being negligible).

Perspectives of adaptation

By classifying samples according to their Sr content, Sr isotope measurements using MC-ICPMS at LSCE are routinely applied to Sr-rich samples, *i.e.* with Sr as a major element (wt.%) or minor element (ppm). Our research into an application on linseed oil and colophony samples provided the opportunity to test the established protocols on Sr-poor samples, *i.e.* with Sr at trace and ultra-trace levels (a few ppb or lower).

- Sr isotope measurements are routinely performed on Sr-rich samples in the wt.% or ppm range (goat teeth, leaves, soils, etc.). The linseed oil and colophony samples provide the opportunity to test the established protocols with Sr at trace and ultra-trace levels (\leq ppb).

3. Obstacles overcome and expected

3.1. Overcome obstacle 1: $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the soil bioavailable fraction

Here, the problem was overcome by using a specific chemical treatment on the sampled soils that releases only the bioavailable fraction, keeping the non-bioavailable fraction undissolved (Blum et al., 2000; Knudson et al., 2014). This method is based on the idea that bioavailability can be mimicked by a gentle chemical treatment, milder than one that dissolves all the strontium elements. This treatment, performed with ultrapure chemical reagents in a clean lab to limit laboratory contamination, proceeds as follows: i- combustion at 800°C during 10h, ii- $\text{CH}_3\text{COONH}_4$ 10 mL 1M during 24h (room temperature), ii- collection of the supernatant and evaporation.

3.2. Expected obstacle 2: $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in pine resin

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio may vary in the different organs of pines (roots, bark, needles, resin) due to biochemical reactions. Few studies include measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in pine resins (Kochergina et al., 2021). To validate the conservation of the $^{87}\text{Sr}/^{86}\text{Sr}$ signature from the bedrocks to the pine resin, a corpus of soil-pine resin couples from well-defined locations and tree species was collected through a participatory science survey.

3.3. Expected obstacle 3: non-local Sr contamination

Different possible sources of natural or anthropic non-local strontium such as fertilizers, dust, sea-spray on coastal pines, etc. may impact the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of pine resin (Knudson et al., 2014) and they are taken into account when the geographical provenance of the pine products is known.

Strontium pollution by anthropic activities in the historical production centres of resinous products before the 19th c. is poorly documented, however it should be limited according to current knowledge on past practices ([Chapter 1, § 3.4](#)).

3.4. Expected obstacle 4: isotopic fractionation during the distillation step that separates colophony and turpentine

To our knowledge, the impact of distillation equipment on the final Sr isotopic signature of colophony has not been studied. Colophony and turpentine are products processed from pine resin. As the chemical element Sr is not volatile, the Sr content is expected to tend to zero in turpentine as the distillate of pine resin. Indeed, the boiling temperature required during the distillation process (around 150°C, Hartwig, 2019) is lower than the vaporisation temperature

of Sr (around 1380°C, ILO International Chemical Safety Cards (ICSC)⁵⁵). Then, the isotopic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is expected to be conservative between pine soil and colophony as the distillation residue of the process.

3.5. Expected obstacle 5: $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in linseed oil/colophony varnishes

Early recipes of linseed oil/colophony varnishes involved a mixture of organic binders, with linseed oil assumed to have a minor influence on the final $^{87}\text{Sr}/^{86}\text{Sr}$ value, unlike colophony which can have distinct terroir sources. The Sr isotopic signature was analysed on lab-prepared linseed oil/colophony mixtures to assess the contribution of each.

Early varnishes may also include pigments and/or driers. Inorganic materials added to varnishes might affect the local $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the organic binder since Sr is highly mobile in solution. For example, Nakagawa et al. (2019) showed that charcoal used as black pigment provides a higher content of Sr in Asian lacquers. Similarly, 18th-c. European lacquers contain linseed oil and colophony with a heterogeneous mixture of pigments (Cattersel, 2019). The pigment charge was much lower (or even absent) for early linseed oil/colophony varnishes in violin making, and the addition of a siccativ such as lead white was not systematic (Échard, 2010). Upstream material characterization is necessary prior to considering an application on historical oil/resin varnishes.

3.6. Expected obstacle 6: $^{87}\text{Sr}/^{86}\text{Sr}$ ratio threshold of detection

Sampling cannot exceed the microscale in the field of Cultural Heritage science. Thus, the size of samples is an obstacle to obtaining a clear strontium isotopic signal while preserving the integrity of early objects. In addition, the Sr content in historical materials has to be rich enough (a few ~ 10 ppb) to allow the isotopic measurement to be performed properly. This obstacle requires adapting current Sr isotopic protocols and measurement conditions:

- i- reducing contamination by lowering the level of blanks (choice of containers, quality of the chemicals, choice of protocol between micro-waves, chemical digestion, combustion),
- ii- evaluating the minimum amount of sample to obtain a signal according to the Sr concentration in materials,
- iii- setting the MC-ICPMS to optimum sensitivity and evaluating the uncertainties of measurement of a few-ppb Sr solutions.

4. Initial experimental program

Experimentation 1 – $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in colophony

Industries, violin makers and museums were contacted to collect different types of colophony (Appendix 6 – § 1) (Figure 109). One of the samples was collected in abundant amounts at the Musée de la musique and was defined as the standard. This colophony was supplied by ©Laverdure in the 1980s and produced in the Landes as confirmed by Sr isotopic analyses.

Experimentation 2 – $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the pine soil-resin system

⁵⁵ <https://pubchem.ncbi.nlm.nih.gov/compound/Strontium#section=Boiling-Point>

A participatory science initiative was launched to collect pine soil-resin couples from defined localizations and from the tree species commonly used for colophony production (Appendix 6 – § 1). The call was broadcast on the website of the Philharmonie de Paris in French and English from April to July 2020 during the Covid-19 pandemic. It was also relayed by the National Music Museum in Vermillion (South Dakota), the Stable Isotope Ecology group, the Société Française des Isotopes (SFIS)'s network and the LinkedIn application:

<https://philharmoniedeparis.fr/fr/magazine/breves/pins-et-confinement>

<https://philharmoniedeparis.fr/fr/magazine/breves/pines-and-quarantine>

The collected samples were labelled and classified in a table (Appendix 6 – § 2) (Figure 109). Some typical soil-resin couples were selected for Sr analyses according to the geographical origin and the tree species. Several measurements were duplicated to test the reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the soil-pine resin couples. Each Sr isotopic measurement on samples with a well-identified geographical provenance was compared with extract expected Sr values in isoscapes.

Experimentation 3 – $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the pine soil-resin-colophony system

Colophony with a well-defined geographical provenance is often difficult to identify on the current market due to mass production. However, efforts were made to identify and contact companies with local production to collect pine soil-resin-colophony trios (table with contacts in Filemaker, Appendix 6 – § 1.2) (Figure 109). Soil, resin and colophony from the same provenance were individually analysed to compare their $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and verify the absence of fractionation or non-local contamination.

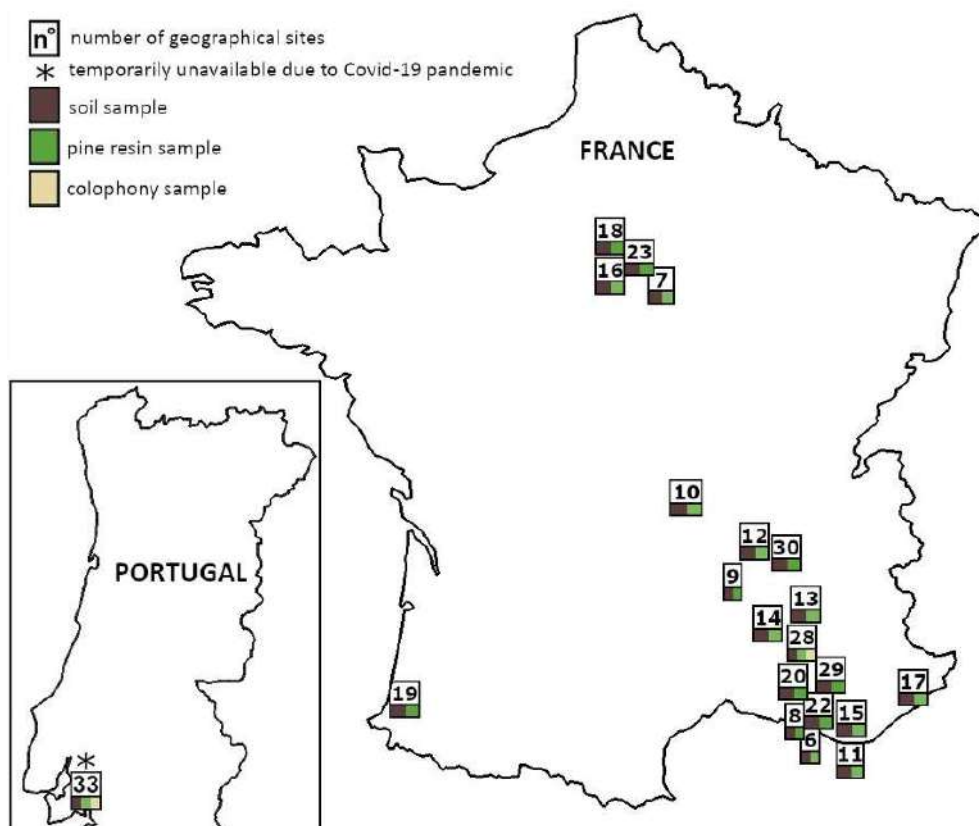


Figure 109. Survey of colophony, soil/resin duo and soil/resin/colophony trio.

Experimentation 4 – $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in resin-oil mixture derived varnishes

Feasibility tests of $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic mixing were carried out on a combination of colophony and linseed oil for which the Sr isotope ratio of each compound was previously measured separately. We assumed that the Sr content in colophony would be the major contributor and an indicator of geographical provenance, but this assumption had to be verified.

Varnishes were prepared in the laboratory with selected linseed oil and colophony samples (Table 38):

- i- selection of previously analysed colophony
- ii- Sr analyses of linseed oil
- iii- Sr analyses of lab-prepared varnishes

We also planned to verify that the Sr level in turpentine (MGD104) was the same as in blanks.

In the meantime, the lab varnishes were also analyzed using radiocarbon dating to compare fresh and dry varnish films and linseed oil/colophony mixtures with a significant age difference. Linseed oil and a colophony produced during the bomb peak were mixed with linseed oil and colophony with a lower ^{14}C content.

Table 38. Composition of the varnishes prepared in the laboratory

Varnish ID	Colophony			Linseed oil		
	sample ID	mass (mg)	$^{87}\text{Sr}/^{86}\text{Sr}$	sample ID	mass (mg)	$^{87}\text{Sr}/^{86}\text{Sr}$
MGD45	MGD25	350.3	0.7100	MGD38	849.5	0.7105
MGD46	MGD22	828.0	-	MGD31	-	-
MGD47	MGD21	400.8	0.7133	MGD31	825.7	0.7105

5. Protocols, problems and adaptations

The experiments presented below are organized according to the different problems to be solved rather than the chronological order. The successive adaptations of protocols are shown in boxes with bullet points at the end of each step.

A summary table (Table 41) of the analyses, with reliable results that can be used, is provided at the end of the section.

5.1. Protocols for soils

Strontium extraction from soil is common. At the LSCE, we adapted the protocol previously published by (Blum et al., 2000; Knudson et al., 2014) that discriminates between total strontium and bioavailable strontium.

Protocol F: - Combustion of soils in an oven at 800°C during 10h.

- 10 mL of ammonium acetate 1M to 1g of soil for 24h at room temperature
- Take up the supernatant and evaporate the solution at room temperature under a class 100 laminar flow hood in a class 1000 clean room.

The preparation of soil samples for Sr isotope measurements was applied on 1g according to the well-established protocol F ([Appendix 6 – § 3, C. Gauthier](#)). The difficulties encountered with linseed oil, colophony, pine resin and varnishes due to the sample size do not apply to soil samples because they are Sr-rich and available in large quantities.

- Sr bioavailable fraction was separated from the soil matrix following a proven protocol (see protocol F).

5.2. Adaptation of protocols

Protocols to release strontium before ICP-MS and MC-ICPMS measurements firstly consist in removing the organic material, also called "mineralisation procedure" (digestion, combustion,...), followed by the chemical separation of strontium from other elements (elution) as previously described in [§ 2.4](#). Blank and internal references were included in the whole procedure including the common NBS 987 Sr isotopic standard solution with a reference value of 0.710245 and the JCT standard, a marine carbonate (Giant Clam powder) with a value representative of the actual ocean signature (0.709165 ± 0.000012 , (Lazareth et al., 2016; Weber et al., 2018)).

5.2.1. Digestion methods

Several mineralisation procedures are available to remove the organic fraction of pine products and linseed oil: 1-microwave digestion, 2-acid digestion or 3-combustion ([Appendix 6 – § 3](#)). Microwave digestion was not investigated due to the lack of suitable containers. Acid digestion was tested as follows on colophony (MGD21), turpentine (MGD104), pine resin (MGD105) and linseed oil (MGD31 and MGD38):

Protocol A: Cleaned Savillex™ beakers were rinsed three times using successively 0.5 M HNO₃ and MilliQ water. The samples were weighed directly in the Savillex™ beakers and dissolution with ultra-pure chemicals, 5mL 8M HNO₃ and 5mL 30% H₂O₂, was carried out to break the organic matrix. The samples in the Savillex™ beakers were heated overnight at 120°C on a hot plate.

* As the chemical mixture is explosive for MGD104 (strongly exothermic), the amount of chemicals required for complete mineralisation of the other samples in a sufficient concentration of Sr is too high. Thus, the protocol was unsuccessfully applied on the tested samples.

* The acid digestion protocol was abandoned for the preparation of these biological samples.

- The acid digestion protocol is the protocol used for soil material but was abandoned for biological and manufactured pine materials.

5.2.2. Combustion conditions

Protocol B: The crucibles were pre-cleaned with three successive rinsings with 0.5 M HNO₃ and MilliQ water. The samples were weighed in lidded porcelain crucibles. Then, the samples were reduced to ash in an oven to break down the organic matter. The initial temperature was 70°C with heating ramps of up to 80 °C every 20 min to a maximum temperature of 300 °C (caution: burning point of plants), and finally with heating ramps of up to 80 °C every 40 min to a maximum temperature of 550 °C. After combustion, the samples were taken up from the crucibles with 4mL of 4 M HNO₃.

* The protocol was applied on colophony (MGD21), pine resin (MGD105), bark (MGD39E), linseed oil (MGD31, MGD38) and turpentine (MGD104).

* Turpentine and pine resin samples, which contain a fraction of turpentine, can strongly degas. It is therefore very important to ensure a very efficient smoke extraction in the oven (extraction directly from inside the oven).

* The speed of the heating ramp was too fast for linseed oil and turpentine samples. Linseed oil overflowed the crucibles, increasing the probability of contamination.

Protocol C: The crucibles were pre-cleaned with three successive rinsings of 0.5 M HNO₃ and MilliQ water. Linseed oil, turpentine and varnish samples were weighed in the covered porcelain crucibles. The initial temperature of the oven was 70°C with heating ramps of up to 80 °C every 30 min to a maximum temperature of 150°C, followed by heating ramps up to 80 °C every 60 min from 150°C to 310°C (caution: burning point of natural oils at 250°C and around 150°C for turpentine). The final stage was heating ramps up to 80°C every 30 min from 310°C to 550°C. After combustion, the samples were taken up from the crucibles with 4mL of 4 M HNO₃.

* protocol C worked well with the manufactured samples (linseed oil, turpentine and varnish).

- The mineralisation step of the organic fraction of pine resin, pine bark and colophony was performed by combustion in an oven following a heating ramp of up to 240°C/hour, while a slower heating ramp (160°C/hour) was chosen for the turpentine and linseed oil samples following protocol C.

5.2.3. Selection of containers

The Sr content in colophony is at trace level and required a careful check of the blank levels of all chemicals and containers to secure the interpretation of the isotopic strontium ratio. Too high a Sr contamination of the crucibles could be due to alteration of the porcelain, uncleaned exogenous Sr from previous experiments and dust particles.

Crucibles, Savillex™ beakers and borosilicate glass tubes

The crucibles, Savillex™ beakers and glass tubes were pre-tested using ICP-MS, in order to sort them and to discard those that were contaminated, after being subjected to cleaning and leaching according to protocol D. Containers that yielded less than 0.1 ppb of Sr were considered as contamination-free. The limit of detection for measurements of Sr content using ICP-MS here was 50 ppt.

Protocol D: The lidded porcelain crucibles are pre-cleaned with three successive rinsings with 3M HNO₃ and MilliQ water between each subsequent test:

- * Test 1: 5mL 3N HNO₃ in covered crucibles at 80°C 1h on a hot plate.
- * Test 2: 5mL 3N HNO₃ in uncovered crucibles at 80°C 1h on a hot plate.
- * Test 3: 10mL 0.5N HNO₃ in uncovered crucibles at 80°C 1h on a hot plate under a class 100 laminar flow hood in a class 1000 clean room.
- * Test 4: 5mL 0.5N HNO₃ in uncovered crucibles at 80°C 1h on a hot plate under a class 100 laminar flow hood in a class 1000 clean room.

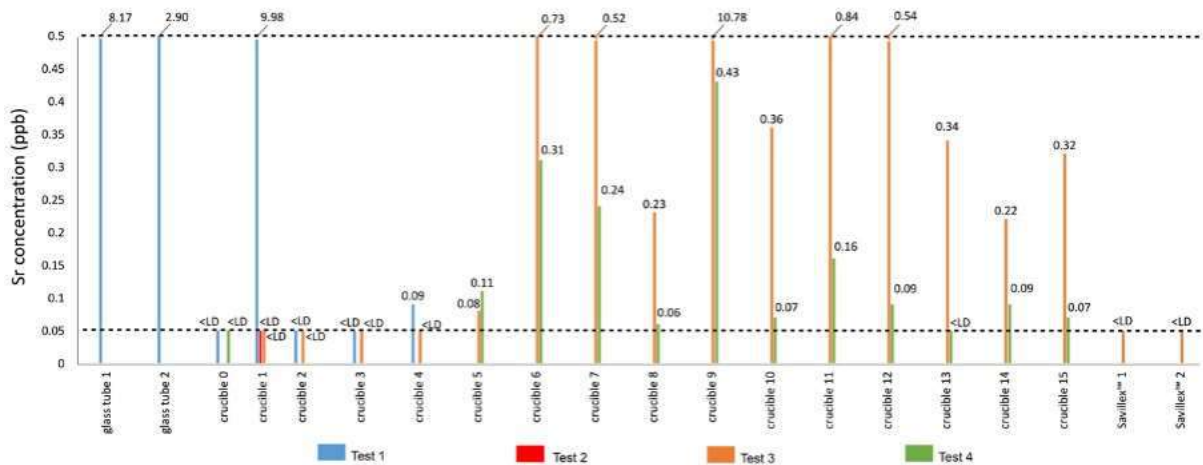


Figure 110. Sr concentrations of uptake solutions measured using ICP-QMS after cleaning and take up steps of crucibles, lids, Savillex™ containers and glass tubes (with relative error of 5%). <LD is for "below the limit of detection of 0.05 ppb".

The following conclusions can be drawn from the results on blank evaluation:

- * The borosilicate glasses used to produce oil/colophony lab-varnishes leach Sr in high concentrations, and are therefore unsuitable for Sr isotope analyses.
- * The crucible lids can be a source of contamination due to the condensation of the solution at 80°C on the hot plate. The same problem occurs if the solution percolates on the edge of the crucibles.
- * The experimental conditions were optimized under a class 100 laminar flow hood in a class 1000 clean room.
- * Savillex™ containers do not release exogenous strontium, but they were not used in the following experiments because they are unsuitable for digestion by combustion.
- * The successive cleanings and leachings were insufficient for some crucibles that continued to release Sr due to the porcelain weathering (surface alteration with time).
- * Only the lidded crucibles with an Sr content less than 0.1 ppb were selected for the following isotope analyses.

Comparison with aluminium crucibles

To further qualify the crucibles, a test applied on a blank and MGD31 (linseed oil) sample was performed using MC-ICPMS with a selected porcelain crucible whose inner surfaces were

covered with aluminum foil (Figure 111). The test clearly showed that adding aluminum foil in the crucible enables a good blank to be obtained.



Figure 111. Comparison of MC-ICPMS $^{87}\text{Sr}/^{86}\text{Sr}$ results on blank and MGD31 (linseed oil) sample digested by combustion in pre-cleaned lidded porcelain crucibles covered with aluminium foil or not.

- Borosilicate glasses used for linseed oil-colophony varnishes are not suitable for Sr isotopy.
- We recommend using here lidded porcelain crucibles in good condition and systematically pre-cleaning them with three successive rinsings of 0.5 M HNO_3 and MilliQ.
- We selected porcelain crucibles that provided a low Sr content in blanks after pre-measurements using ICP-MS.
- The addition of an aluminium foil inside the porcelain crucibles was tested to obtain a better level of blank for pine products and linseed oils. This indicates that other tests need to be further performed with Al/metal crucibles when using the combustion protocol.

5.2.4. Method to take up the ash samples after combustion

The lidded porcelain crucibles were pre-cleaned with three successive rinsings of 0.5 M HNO_3 and MilliQ. Analyses on MGD21 colophony were duplicated in the pre-selected porcelain crucibles (part 5.2.3) with two methods to take up the samples from the crucibles after combustion:

- Protocol E: - Protocol E-1: take up with 5mL 0.5N HNO_3
 - Protocol E-2: take up with 2mL of MilliQ water

The Sr concentration in the crucibles was measured using ICP-MS and the results showed that method n°1 takes up a higher concentration of Sr than method 2 from the same crucible (Table 39). The use of 5mL 0.5N HNO_3 was initially chosen to optimize the collection of the Sr from samples; however, a fraction was leached from the porcelain crucibles. Thus, protocol E-2 was finally chosen for the preparation of the following samples by leaching crucibles with a minimum volume of MilliQ quality water, limiting Sr contamination by the porcelain.

- To optimise the protocols, the mineral fraction of ash samples was taken up from crucibles with 2 mL of MilliQ water (protocol E-2) rather than 4mL of 4 M HNO_3 to avoid leaching Sr from the porcelain walls of the crucibles.

Table 39. ICP-MS results following methods 1 and 2 to take up ash samples in crucibles initially filled with about 2 g of MGD21 colophony and also evaluated in the empty crucibles (blank)

Crucibles	Method 1 (take up with HNO ₃)		Method 2 (take up with water)	
ID	Content (mg)	Sr concentration (ppb)	Content (mg)	Sr concentration (ppb)
crucible 0	-	0.011	-	-
crucible 1 + MGD21	2101	21.08	2097	12.02
crucible 2	-	0.28	-	0.08
crucible 3	-	0.18	-	0.03
crucible 4	-	0.01	-	0.00

5.3. Minimum size of samples to be analyzed

Kochergina et al. (2021) determined that Sr concentrations in soil samples range from 6.6 to 861 ppm and are a few ppm in pine needles, barks and cones. Although Honda et al. (2016) and Lu et al. (2015) did not publish the results, raw lacquer sap contains strontium at a concentration of about 0.6 to 2 ppm, whereas drying oils yielded results of 20-100 ppb (personal communication). Thus, pine bark, needles and soils are considered as Sr-rich samples for which the routine protocols at the LSCE are suitable. On the contrary, we considered colophony and linseed oil as Sr-poor samples. Different protocols, already available for Sr-rich plants ([Appendix 6 – § 3, protocol C. Gauthier](#)), were tested on Sr-poor pine resin, colophony and linseed oil to estimate their concentration and define the minimum sample size for isotope measurements.

Colophony samples

Three starting masses (200, 500, 1000 mg) of colophony MGD21 were treated according to protocol B (slow oven temperature ramp) with the ashes taken up from porcelain crucibles with 4mL of 4 M HNO₃. The resulting Sr concentrations were measured using ICP-QMS and the mean Sr content calculated from the 3 aliquot values (Table 40) was relatively homogeneous at about 60 ± 16 ppb in the colophony samples (Table 40). For information, the limit of detection was 0.05 ppb during the Sr content measurements using ICP-MS.

Table 40. Protocol B. MC-ICPMS measurements for different tested weights of MGD21 colophony

Sample ID	Lab ID	Weight (mg)	Average Sr (µg/kg)
MGD21	8298	201.7	47.76
MGD21	8297	501.8	52.60
MGD21	8296	1008.9	77.66

In our configuration, the final solution after elution must be at least 1 ml and 2 ppb in Sr in order to undertake measurements using the MC-ICPMS NEPTUNE Plus. However, the nominal Sr concentration for an optimal isotope measurement precision is usually 20 ppb at the LSCE.

We therefore determined the minimum initial size of colophony samples as 1g since it was estimated by calculation that for 1 g of MGD21 colophony with an initial Sr concentration around 60 ppb (Table 40), and an elution volume of 2.5 mL, the final volume of 1ml would contain 24 ppb in Sr which is above the optimal Sr content of 20 ppb.

Linseed oil samples

MGD38 and MGD31 linseed oil samples were analyzed using MC-ICPMS: the Sr content in linseed oil samples was estimated by calculation considering a realistic yield of 100% during chemistry.

The MGD31 sample had an initial volume of 5 mL, and the final solution had an estimated Sr concentration of 24 ppb after elution in a volume of 2.5 mL. Thus, the calculation provides a Sr concentration of 12 ppb in MGD31 linseed oil.

The MGD38 sample had an initial volume of 5 mL, and the final solution had an estimated Sr concentration of 20.3 ppb after elution in a volume of 2.5 mL. The sample was dissolved 5.72 times, so the calculation provides an initial concentration of 58 ppb in MGD38 linseed oil.

To conclude, we determined a Sr concentration of 60 ppb in colophony and an estimated average of 30 ppb in linseed oils if a yield of 100% is considered (which means no Sr loss during chemistry). For linseed oil samples, we chose a sampling volume of 5 mL to reach the optimal Sr content (20 ppb) for precise isotopic measurements of Sr. For Sr isotope measurements, 1 g minimum of colophony, pine resin and bark, 1g of soil, and 5 mL of linseed oil were used with the protocols.

5.4. Sr purification and elutions

Once the samples had been rid of the mineral components, the remaining matter followed the elution step. This step was conducted under a class 100 laminar flow hood in a class 1000 clean room (clean lab).

A cleaned Teflon column charged with a SrSpec (Eichrome Inc.) resin was alternately pre-cleaned as follows:

3x 1mL 3 M HNO₃

3x 1mL MilliQ water

Then the mineralized sample is taken up in a 3 M HNO₃ solution (4 mL) and 1 mL per 1 mL is loaded on the top of the cation exchange column. Elution occurs as follows:

3x 1mL 3 M HNO₃ to elute major elements present in the solution (e.g. Ca)

5x 500 μ L ultra-pure MilliQ water to elute Sr fixed on the resin in nitric conditions in order to obtain 2.5 mL of purified Sr solution in MilliQ medium.

5.5. Optimized protocols for soil, pine resin, pine bark, colophony, and linseed oil

Below is a summary diagram of the selected protocols according to the nature of the samples (soil, bark, resin, colophony, linseed oil) (Figure 112).

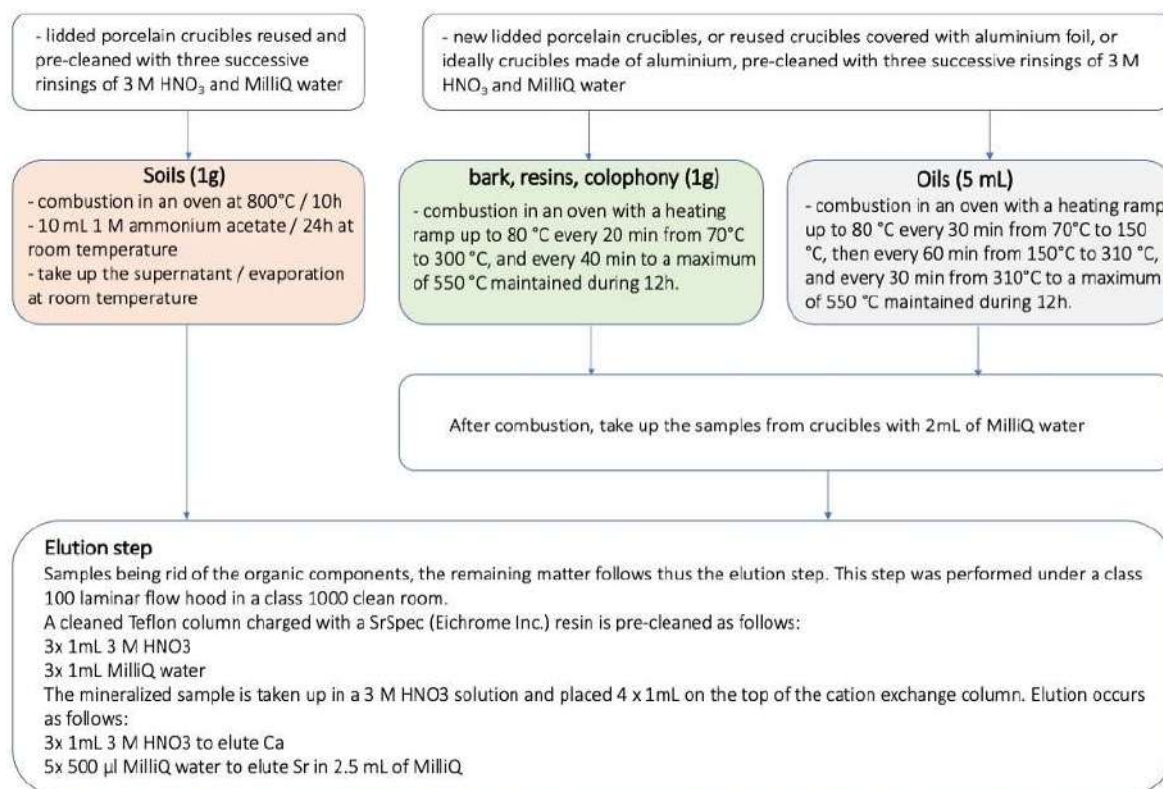


Figure 112. Sum up of the protocols for soil, pine bark, resins, colophony samples and linseed oil samples.

6. Results: samples run under optimal protocols

The optimization of the protocols was carried out as problems appeared. Several samples were redone under increasingly suitable conditions. However, we could not analyze all the samples collected due to lack of time or equipment, nor obtain valid results for some measured samples such as the "artificial varnishes" prepared and analyzed for ^{14}C investigation only (Chapter 3 – § 5).

All the treatments carried out are detailed in Appendix 6 – § 4. Here, only the chemical treatments that led to reliable measurements are listed. Unfortunately, they represent less than half of the chemistry and measurements performed.

The limited number of usable values notably limits the investigation as only 20 replicable results were obtained for 38 analyses. There remains only:

- 2 soil-resin couples out of the 4 analyzed couples and 1 soil-bark couple
- 1 soil-colophony couple, but no soil-resin-colophony trios
- none of the lab-prepared varnishes
- no turpentine samples
- 5 colophony samples
- 2 linseed oil samples out of the 3 analyzed

Validated measurements are shown in Table 41 and illustrated in Figure 113. All the results are reported in Appendix 6 – § 5.

Table 41. Summary of the samples with valid MC-ICPMS measurements. (nd: not determined) [1] provided by Mr Denis Caban, lutherie workshop Orléans.

Site ID	Location	Geographical coordinates (Lat./ Long.)	Material	Sample ID	Lab ID	$^{87}\text{Sr}/^{86}\text{Sr}$ ratio	mean	2 σ	$\Delta^{87}\text{Sr}/^{86}\text{Sr}$ (plant product/soil)
6	Marseille (13)	43.252222 / 5.372500	pine bark	MGD39E	June 2020	0.7084	0.7083	0.00013	0.0002
					9090	0.7083			
			soil	MGD40	June 2020	0.7081			
12	Saint-Etienne (42)	45.411944 / 4.435000	pine resin	MGD54	9082	0.7164	0.7171	0.00065	- 0.0013
			soil	MGD55	June 2020	0.7177			
28	Propiac (26)	44.279176 / 5.240658	colophony	MGD107	9089	0.7091	0.7084	0.00075	0.0015
			soil	MGD108	June 2020	0.7076			
19	Landes (40)	43.5625 / - 1.357778	pine resin	MGD74	9081	0.7091	0.7093	0.00020	- 0.0004
			soil	MGD75	June 2020	0.7095			
20	Avignon (84)	43.635500 / 5.162444	soil	MGD77	June 2020	0.7084	-	-	-
1	Les Landes (40)	nd	colophony	MGD21	8415	0.7135	0.7135	0.00012	-
					8416	0.7133			
					June 2020	0.7136			
3	nd [1]	nd	colophony	MGD25	9087	0.7100	-	-	-
21	Besançon (25)	nd	colophony	MGD90	9083	0.7106	-	-	-
26	Portugal	nd	colophony	MGD103	9088	0.7164	-	-	-
5	Netherlands	nd	linseed oil	MGD31	9093	0.7117	0.7111	0.00059	-
					9097	0.7105			
32	Canada	nd	linseed oil	MGD38	June 2020	0.7105	0.7105	0.00005	-
					9094	0.7104			

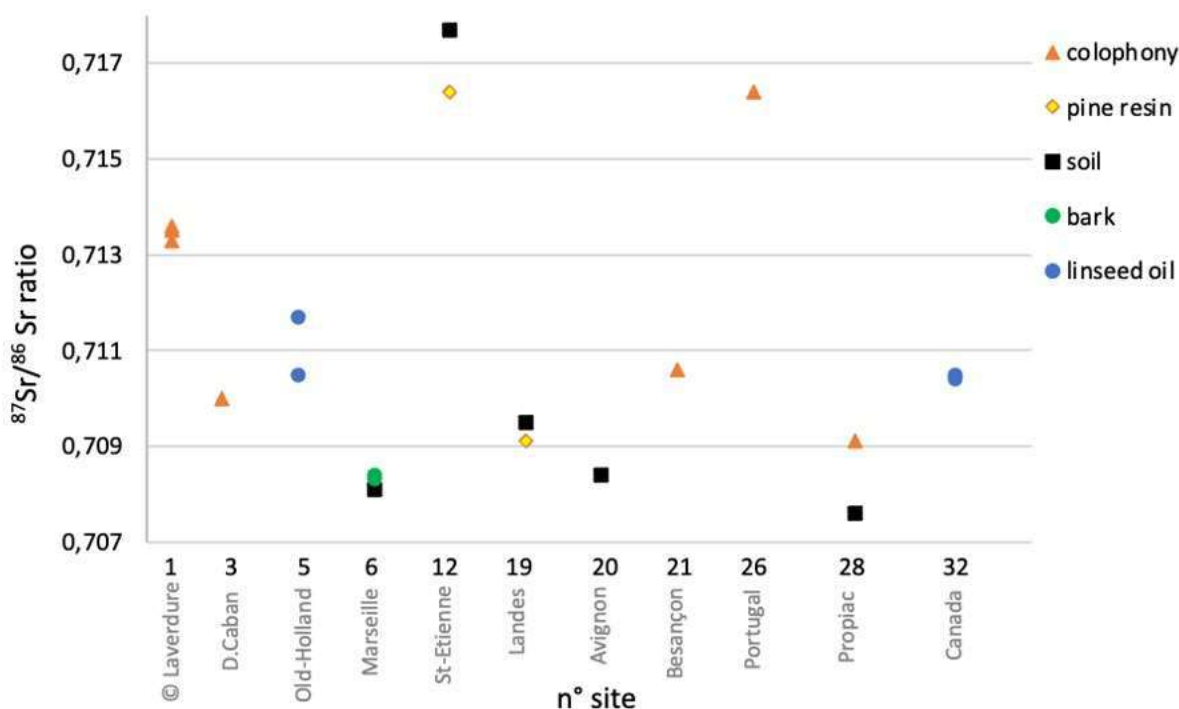


Figure 113. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of usable MC-ICPMS results obtained on pine products and soil depending on the origin. The standard deviation in ppm at 2σ (<20 ppm) is hidden by the size of the markers.

7. Discussion

7.1. Analytical aspects

Protocols for trace and ultra-trace samples

Sr isotope measurements using MC-ICPMS are routinely applied to Sr-rich samples (wt.% or ppm levels) at the LSCE (§ 2.4). The protocol for soils (~ppm) (Protocol F, § 5.1), which was previously appropriated by the team, was successfully applied in this study and showed good agreement between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio values from soil samples (Table 41) and isoscapes (Table 42).

It was found, however, that the routine protocols needed to be adapted for our research involving pine products and linseed oil with Sr at trace level (~ppb) since the porcelain crucibles used during the digestion step induced Sr contamination. This has an impact on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at the 3rd digit after the decimal point for Sr-poor samples (Appendix 6 – § 5), whereas routine Sr isotope measurements at the LSCE usually provide an accuracy to the 5th/6th digit after the decimal point for Sr-rich samples. A possible solution is to replace porcelain crucibles by aluminum crucibles (Figure 111). We also showed that the borosilicate glasses used to produce oil/colophony lab-varnishes at the Musée de la musique release Sr in even higher concentrations than porcelain crucibles, and are therefore unsuitable for Sr isotope analyses (Figure 110). Due to the time-consuming protocols, it was not possible to repeat the Sr measurements on linseed oil/colophony varnishes made in Sr-free containers.

We managed to identify how to reduce Sr contamination during the mineralization step prior to Sr chemical separation, and we evaluated the minimum sample size of colophony and linseed oil for Sr isotopic analyses, which is a crucial issue in Cultural Heritage sciences to assess the potential of the method on studying early linseed oil/colophony varnishes. According to the current technological configuration using the MC-ICPMS NEPTUNE Plus at the LSCE, 1 g of colophony and 5 mL of linseed oil are the minimum sample size required for precise Sr isotope measurements. Thus, a minimum of around 1 g of linseed oil/colophony varnish is today necessary for Sr isotope measurements (Table 38). The minimum values do not correspond to a setting of the MC-ICPMS at the limit of sensitivity, but to the limit for the reliable reproducibility of Sr isotope measurements. Preliminary MC-ICPMS tests were recently performed to measure Sr isotopes at lower concentrations using standard solutions and initial results indicated that the analytical uncertainty remains below 20 ppm for Sr contents in solution of 5 ppm, and around 100 ppm for 1-2 ppb Sr solutions. Consequently, one way to decrease the initial material needed is to develop Sr isotope measurements at lower Sr concentrations at the LSCE, for example using injection loops and/or a d-DIHEN direct injection system adapted for MC-CPMS as already tested positively for other elements (Louvat et al., 2019).

Interpretation - reproducibility of measurements

The results showed clear tendencies regarding the reproducibility of measurements. Duplicate measurements on pine bark (MGD39E, site 6, Marseille), colophony (MGD21, site 1, ©Laverdure) and linseed oil (MGD31, site 5, Old-Holland and MGD38, site 32, Canada) enabled us to specify the interpretation limit of the approach. It was found that measurements are reproducible at ± 0.0001 for pine bark (MGD38E: 0.7083, 0.7084), ± 0.0002 for colophony (MGD21: 0.7133, 0.7135, 0.7136) and better than ± 0.0006 for the Sr-poor linseed oil (MGD31: 0.7105, 0.7117 and MGD38: 0.7104, 0.7105) (Table 41). The reproducibility is obviously impacted by the initial Sr content for 1g of material which is higher for pine bark (~ppm) than for colophony, and even lower for linseed oil (~ppb).

Reference material

The MGD21 sample of ©Laverdure colophony produced in the Landes could be used as a potential standard due to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio values which are close to the regional isoscapes of the literature around 0.713 (Appendix 6 – § 6, Table 42) and because of the large quantity available. It comes out at 0.71347 ± 0.00012 (standard deviation) with a reliable reproducibility of the measurements (Table 41). As a first step, these results support the feasibility of attributing a branded colophony used at the Musée de la musique to its terroir of production in France.

7.2. Conservation of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio in the strontium cycle: soil-resin duos and soil-resin-colophony trios

The validated measurements comprise portions of the strontium cycle in order to evaluate the absence or presence of natural isotope fractionations:

Site 6, Marseille: soil → pine bark

Site 12, Saint-Etienne: soil → pine resin

Site 19, Landes: soil → pine resin

Site 28, Propiac: soil → colophony

Unfortunately, after data validation, complete soil-resin-colophony trios were not available. The values are listed in Table 41 and illustrated in Figure 113. However, although the number of valid results is too limited to support a detailed statistical study, some tendencies can be observed (Table 41):

soil → pine bark: the data suggest a conservation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio between soil and pine bark. For instance, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in pine bark from site 6, Marseille, with a reliable reproducibility of the measurements at 0.0001, has only a low enrichment in comparison with the soil ratio, i.e. $\Delta^{87}\text{Sr}/^{86}\text{Sr} \sim 0.0002$.

soil → pine resin: A depletion of -0.0013 was observed between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of soil and pine resin from site 12, Saint-Etienne. The depletion was measured at -0.0004 between soil and pine resin from site 19, Landes. The origin of the depletion can be attributed to operational difficulties faced during the adaptation of the protocols for samples with Sr at trace level. Additional measurements on new sample duos, or by duplicating previously measured samples, are necessary to confirm the conservation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio between soil and pine resin and invalidate a systematic fractionation.

soil → colophony: Sr isotope measurements were validated on soil-colophony couples from site 28, Propiac, i.e. at the beginning of the Sr cycle and at the end of the transformation process of pine resin into colophony (before its use in varnishes). The colophony was artisanally produced by Samuel Aubert from the ©Galipot company. An enrichment of 0.0015 between soil and colophony from site 28 was observed. This enrichment cannot be attributed to the distillation process used to obtain colophony, which leaves the turpentine depleted in ^{87}Sr , due to the high vaporisation temperature of Sr (§ 3.4). Further investigation is required using aluminium crucibles in our protocols to reduce contamination.

Our study on the conservation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from soil to colophony is based on the transposition of results obtained with actual materials to early materials. It could also be compared with our current knowledge of former manufacturing practices: the use of fertilizers or not, harvesting processes of pine resin, materials for distillation and preparation of violin colophony or varnishes (Chapter 1 – § 3.4).

7.3. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a tracer of geographical origin

The site-by-site comparison of the range of strontium isotopic data with the IRHUM isoscapes (Appendix 6 – § 6, Table 42) helps assess the potential of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a geographical tracer of origin (Figure 115). This comparison was conducted within the interpretation limit of 3 decimal digits as previously defined.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the samples are close to regional values in isoscapes from the literature for the following sites with an accurately defined geolocation: site 6 (Marseille), 12 (Saint-Etienne), 28 (Propiac), 20 (Avignon), 21 (Besançon), and site 19 in the Landes (Figure 115). Actual colophony samples from ©Laverdure (site 1, Landes), ©Costa&Irmãos (site 26, Portugal), ©Domaines&Patrimoine (site 21, Besançon) and the ©Galipot (site 28, Propiac) companies (from the least to the most accurate origin) are also in agreement with the $^{87}\text{Sr}/^{86}\text{Sr}$

ratio of their production locality found in the isoscapes despite potential Sr contamination during the Sr cycle previously discussed as a potential limit of the method.

Soil and pine bark samples from site 6, Marseille (lat.43.252/long. 5.373) provide $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.7081 to 0.7084, i.e. close to the regional isoscape value of 0.7079 (lat.43.267/long.5.741) (Table 42). The soil sample from site 20, Avignon (lat.43.636/long.5.162) has the same value of 0.7084 as a geographically close isoscape ratio (lat. 43.623/long.5.492). The soil sample from site 28, Propiac (lat.44.279/long.5.241) has a Sr isotope ratio of 0.7076, which is closer to the nearby regional value of 0.7074 (lat.44.111/long.5.944) than for the ©Galipot colophony at 0.7091 from the same site. As the measured values of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in our samples and from regional isoscapes range from 0.7074 to 0.7091, pine products from Marseille (site 6), Avignon (site 20) and Propiac (site 28) cannot be discriminated due to the underlying bedrocks (Table 42, Figure 115).

The soil-resin couple from site 19, Landes (lat.43.563/long.-1.358) yields $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7095 and 0.7091, which are lower than the Landes regional isoscape values (0.711 - 0.714) (Appendix 6 – § 6, Table 42). This could be related to the geographical position of site 19, which is closer to the foothills of the Pyrenees (Figure 115). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the ©Laverdure colophony used as a reference at 0.71347 ± 0.00012 is more consistent with the mean regional value, however.

The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the MGD90 colophony ©Domaines & Patrimoine⁵⁶ from site 21, Besançon, has a value 0.7106, which is consistent with the mean regional value of 0.7110 ± 0.0023 provided by isoscapes in Table 42.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of soil and pine resin samples from site 12, Saint-Etienne (lat.45.412/4.435) in the Massif Central with a value of 0.7171 ± 0.0007 can be clearly differentiated from sites 1 and 19 in the Landes and from site 6, Marseille, site 20, Avignon and site 28, Propiac near the Rhône valley, as well as from site 21, Besançon. As for the MGD103 colophony ©Costa&Irmãos which is a bulk of transformed pine resin from the Beira Litoral and Trás-os-Montes regions in Portugal, it yields a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7164 in agreement with values reported by Hoogerwerff et al. (2019) (Figure 107) and close to regional values in the Massif Central.

⁵⁶ <https://www.domaines-et-patrimoine.fr/fr/carte-de-nos-forets.html> (consulted on 2020/04/05)

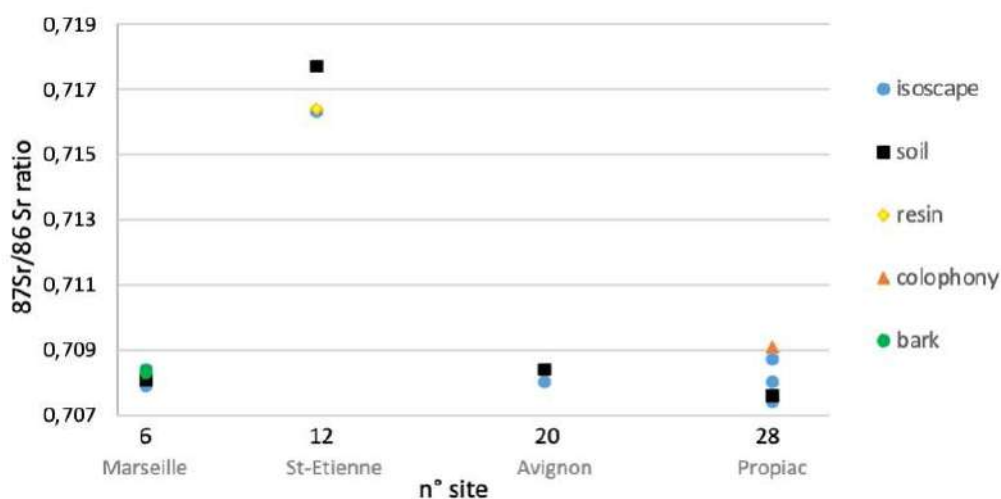


Figure 114. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio obtained for pine products and soils depending on the site. The standard deviation in ppm at 2σ (<20 ppm) is hidden by the size of the markers.

Table 42. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio obtained for pine products - soil couples depending on the origin and compared with values from isoscapes (IRHUM).

Sample ID	Site ID	Location	Geographical coordinates (Lat./ Long.)	$^{87}\text{Sr}/^{86}\text{Sr}$ ratio
*IRHUM-a	A	Marseille (13)	43.267 /5.741	0.7079
*IRHUM-b	B		43.229 /5.806	0.7079
*IRHUM-c	C	Saint-Etienne (42)	45.541 /4.446	0.7163
*IRHUM-d	D	Avignon (84)	43.847 /4.283	0.7080
*IRHUM-e	E		43.623 /5.492	0.7084
*IRHUM-f	F	Drôme (26)	44.111 /5.944	0.7074
*IRHUM-g	G		44.885 /5.143	0.7080
*IRHUM-h	H		44.892 /5.115	0.7087
*IRHUM-i	I	Les Landes (40)	44.11 /-0.619	0.7126
*IRHUM-j	J		nd	0.7135
*IRHUM-k	K		44.126 /-1.22	0.7110
*IRHUM-l	L		43.89 /-0.882	0.7127
*IRHUM-m	M	Besançon (25)	47.307 /6.365	0.7079
*IRHUM-n	N		47.049 /5.357	0.7117
*IRHUM-o	O		46.914 /5.363	0.7135

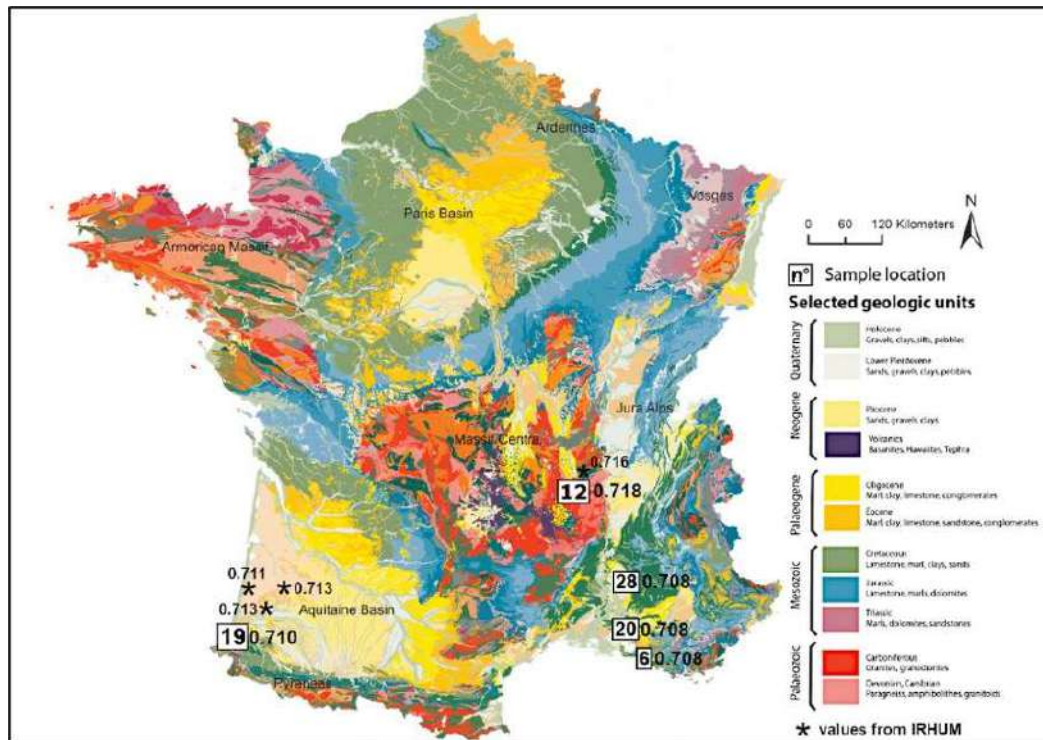


Figure 115. Geological map of France with the distribution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained for soil samples depending on the geographical sites and compared with values from isoscapes (IRHUM).

As a conclusion, we highlight the possibility of discriminating actual colophony from European regions with significant differences in the geological bedrock such as samples from Portugal and the Massif Central in France. According to historical records (Chapter 1 - § 3.4), the production of pine resin was centralized in southern France during the modern period. Further research could be carried out to deepen the historical knowledge on the trade of violin colophony using the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio by cross-linking the geographical location of historical centres of pine production and early renowned lutherie centers (Figure 116).

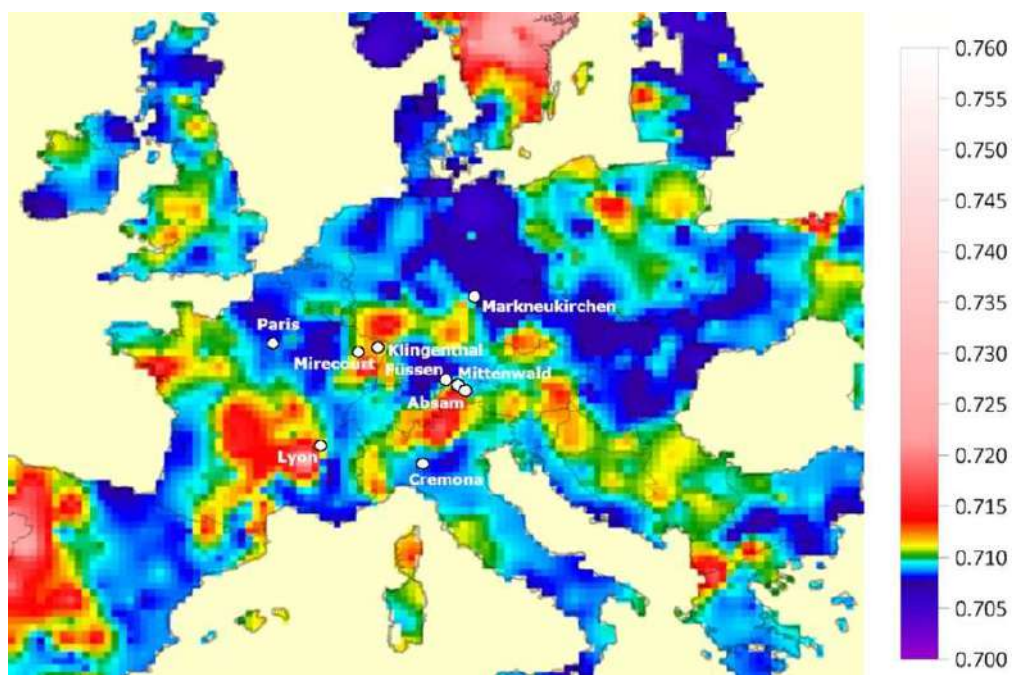


Figure 116. $^{87}\text{Sr}/^{86}\text{Sr}$ modelled map in Europe with several renowned historical lutherie workshops (modified from Hoogewerff et al. 2019).

Lab varnishes were prepared according to the proportion of 30:70 in colophony and linseed oil employed in early varnishes on bowed instruments during the 17th and 18th c. (Weththimuni et al., 2016) (Table 38). Thus, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of linseed oil/colophony varnishes is a combination of the original isotopic signature of each compound. We planned to perform Sr isotope measurements on the lab varnishes in order to evaluate the contribution of the drying oil and the colophony (used as a natural drier) to the final isotopic ratio. However, valid results have not been obtained so far due to (Figure 110):

- i- Sr contamination from the borosilicate glass tubes used for varnish preparation
- ii- Sr contamination from porcelain crucibles during the mineralization of the samples

The protocol problems were part of the process of adapting routine protocols for Sr-rich samples to colophony and linseed oil samples with Sr at trace level (ppb). The origins of the problems were progressively identified and solved, but unfortunately, the strontium isotopic ratio of the lab-made varnishes could not be re-measured for lack of time (Appendix 6 – § 5).

A research perspective is based on the assumption that colophony has a higher concentration in Sr than linseed oil, with around 10 ppb for MGD31 linseed oil from Holland and around 60 ppb for MGD21 colophony from the Landes (§ 5.3). We consequently expect the variability of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in linseed oil/colophony varnishes to mostly reflect the impact of the colophony source.

Moreover, at this stage, we have been unable to discriminate linseed oils using their $^{87}\text{Sr}/^{86}\text{Sr}$ ratio due to the nature of soils used for flax cultivation. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the MGD31 sample of 0.7111 ± 0.00059 provided by Old-Holland Classic Colours at Driebergen (near Utrecht, Netherlands) is associated with the Quaternary sediments covering the Netherlands with values ranging from 0.707 to 0.710 (Hoogewerff, 2010 and Figure 107). The MGD38 linseed oil, which yielded an isotopic ratio of 0.7105 ± 0.00005 , is from an undefined origin in Canada. Nevertheless, the value is in agreement with Quaternary sediments of Toronto and its surrounding area, as indicated on the label of the linseed oil bottle.

From the historical point of view in Europe, the linseed oil from northern France and the Low Countries, which were major production areas during the modern period, had a constant Sr isotopic signature due to the underlying Quaternary sediments (Hoogewerff et al., 2019). Further research applying the protocols adapted for Sr-poor samples during this study, limiting Sr contamination within a lower interpretation limit than 3 decimal digits, will help to validate or invalidate the use of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a tracer of geographical origin of European linseed oil/colophony varnishes.

8. Conclusion

The routine protocols used at the LSCE for Sr-rich samples (wt.% and ppm) were tested and adapted for samples with Sr at trace level (ppb) within the limits of the time and material available. The digestion step proved to be highly complex because of the very low Sr concentration in pine products and linseed oil, and showed that porcelain crucibles are unsuitable due to the release of Sr contamination. Moreover, several difficulties were encountered at this stage due to the nature of turpentine, colophony and linseed oil which were unexpected, ... or maybe not, judging from historical records that mention dreadful accidents in early luthier workshops during the preparation of varnishes. Establishing a reliable

protocol was time-consuming, but also sample consuming. Hence, only a few usable results were obtained: 4 pine product-soil couples, 5 colophony and 2 linseed oil samples, and time was lacking to measure the lab-made varnishes.

This greatly limits the applicability of strontium isotope geochemistry to our samples, and now that the protocol has been established, further analyses have to be done or redone. In the current state of this research, our conclusions are:

- 1- we confirmed that usable results of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured in pine products are correlated with the strontium ratio of the soil bioavailable fraction.
- 2- we established that a minimum amount of 1 g of pine resin and 5 mL of linseed oil is needed for Sr isotope analyses
- 3- MGD21 colophony can be used as a Sr isotopic ratio standard, for samples with a similar matrix
- 4- we highlighted contamination due to porcelain crucibles and dust during the digestion step, and therefore recommend the use of aluminium/metal crucibles and preparation under a class 100 laminar flow hood in a class 1000 clean room.
- 5- we suspect the absence of Sr in turpentine, but could only confirm it indirectly by confirming the conservation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio between soil, resin and colophony.
- 6- we are not yet able to conclude on the relative impact of soil and colophony, whose $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is known, in the final $^{87}\text{Sr}/^{86}\text{Sr}$ signature of a dry oil/colophony varnish. The lab-prepared varnishes have to be redone due the initial problems encountered with the protocols.

However, even if not all the steps were validated, we are confident that the strontium isotopic signature can be used as a tracer of geographical origin for varnishes and other colophony derivatives.

GENERAL CONCLUSION

1. Objectives achieved

General context

Research undertaken to further scientific knowledge about musical instruments, their making, their uses and their restoration still faces unsolved issues on dating and material provenance. Regarding the modern instrumentarium from the 16th c. to the 19th c., current research often provides relevant answers on both aspects by combining dendrochronology, organology, iconographic and written sources, etc. However, the approach has its limits in particular for studying the history of uses of a specific instrument due to the material complexity of musical instruments. The dating and provenance of original materials and the successive modifications-interventions-restorations are still poorly known.

To overcome current scientific obstacles, the aim of this academic study was to explore the feasibility of adapting tools routinely applied on archaeomaterials to materials of modern musical instruments. As the various parts of musical instruments are mainly made of natural materials, it is possible to apply the most advanced techniques of ¹⁴C geochronology and Sr isotope geochemistry, respectively used for dating and provenance studies. The literature is just beginning to highlight the relevance of applying ¹⁴C dating to modern musical instruments (Chase et al., 2009; Durier et al., 2019a) and Sr isotope measurements are emerging for wood provenance studies (Bernabei, 2020). Following thy previous study on wood, this PhD focused mainly on early varnishes as they are more complex organic materials and briefly on gut strings, which are both rich in evidence of historical use practices. The goal of this research was to deepen scientific knowledge and valorize the collection.

State-of-the-art

Among the various organic materials such as wood, glue and gut strings used for stringed instruments, the first decision was to focus on varnishes. The bibliographic research was twofold, exploring historical and physico-chemical approaches that help to contextualize and to apprehend the application of isotope measurements on varnishes and their organic binders. Despite a wide range of early recipes from the modern period, this study mainly concerns linseed oil/colophony varnishes as they were used by the Italian violin Masters of the 17th c. and are the most widely studied varnishes using historical and physico-chemical approaches (Échard, 2010).

The historical state-of-the-art shows that early linseed oil/colophony varnishes were also applied on other Heritage objects. It was decided to broaden the material corpus for ¹⁴C dating application to lacquered pieces of furniture and horse-drawn carriages from the late 17th c. to the early 18th c. The material complexity of varnish stratigraphy formed over time was discussed. The wider socio-economic context around organic binders was explored to consider the possible impacts of the manufacturing and commercial practices of oil-based varnishes and colophony/turpentine ingredients on dating and provenance studies using isotopes.

The state-of-the-art in physico-chemistry highlights the complexity of the molecular and elemental composition of the natural resins commonly used in early oil-based varnishes. This PhD focuses on linseed oil/colophony mixtures but the bibliographic research showed the

feasibility of broadening the isotopic analyses in future research to include other ingredients of natural origin. Gaps in the literature were found regarding the dating and provenance of varnishes and their organic ingredients despite the combination of both historical sources and physico-chemical investigations. Nevertheless, historical and physico-chemical approaches are necessary before combining geochronology and geochemistry as complementary tools of expertise.

¹⁴C dating

- Scientific approach during this PhD

¹⁴C dating is currently underused for dating studies on musical instruments from the modern period. The general methodology for the feasibility tests on varnishes and gut strings during this PhD had to deal with three scientific obstacles: i- the sample size, which cannot exceed a few hundred micrograms; ii- the composite constitutions of the instrument (varnishes, glues, restored parts), which requires specific and complex chemical protocols to extract the carbon to be dated; iii- the modern period, which is not favorable to radiocarbon dating due to complex calibration curves. The main methodological adaptation consisted in microsampling using microsurgical scalpels to mechanically separate varnish layers. The chemical pre-treatments were also optimized to reduce material losses using ice-drying. Microline, EA-GIS or AGE systems were used depending on sample size for extracting purified carbon to be analyzed. ¹⁴C measurements were applied on “bulk” samples with both their organic and inorganic compounds and without pre-molecular separations using solvents due to complex polymeric interactions in dried and aged varnishes.

- Results

After defining a study period initially considered to be the most suitable range of dates for ¹⁴C measurements during the modern period, namely [1600-1730] and [1770-1810], the prospection for a material corpus of application was the next step in this PhD research. Analyses of the corpus highlighted that the mechanical separation of layers was efficient for the isolation of chips from the wooden support, preparation layers, decor layers, surface protective/restoration layers, etc. Sampling protocols and/or chemical treatments were adapted progressively during this study, providing on the one hand ¹⁴C measurements that were consistent with museum expertise (including dendrochronology, material analyses, stylistic comparisons, written sources, etc.), or on the other hand erroneous ¹⁴C results due to the complex organic and inorganic composition of the layers, providing information on making processes or on restoration interventions. ¹⁴C dating was also applied on gut strings, which are often replaced for musical use, and compared with current instrument making expertise and written sources. The results differentiated pre-industrial strings from industrial strings and possibly highlighted different chemical treatments during the Industrial Revolution. Finally, the study using ¹⁴C dating shows that the more knowledge that is available from historical documentation and material characterization, the more suitable the protocol adaptations including chemical treatments and interpretation of the results will be. An example of the equilibrium between information provided by historical documentation, material characterization and ¹⁴C dating is presented in the study case of the Chinese zither qin 18th c. (E.1444) (Durier et al., 2021).

Sr isotopes

- Scientific approach during this PhD

Stable isotopes and the multi-element composition of natural materials are indicators of geographical traceability (Liu et al., 2019). Sr isotope geochemistry was selected during this PhD to trace the origin of organic binders. The general methodology for the feasibility tests, focusing on colophony, was to adapt protocols usually applied on archaeomaterials, to estimate the current minimum sample size for isotope measurements and to verify the absence of isotopic fractionation between soil, pine resin and colophony as a distillation residue of pine resin. Thus, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured on samples of colophony, linseed oil, pine soil/resin duos and pine soil/resin/colophony trios from different provenances mainly in France.

- Results

Sr isotope analyses validated the assumption of the absence of isotopic fractionations between geological bedrock and colophony. The protocol was progressively adapted during the study due to successive pitfalls. For example, the initial protocol induced contamination as Sr is at trace level in colophony, whereas Sr is at major or minor level in commonly analyzed soils, leaves and barks. Finally, the results were conclusive and it was demonstrated that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio could be used to discriminate samples from regions with significant differences in geological bedrock.

To sum up, the aim of this PhD study was to test the feasibility of examining complex organic materials on musical instruments at the isotope scale using the most advanced techniques available at the LSCE and to compare the results with current scientific knowledge gathered using the approaches commonly employed at the Musée de la musique (written sources, dendrochronology, stylistic comparison, etc.). During this research, both early varnishes and gut strings were investigated as testimony of the material history of musical instruments. Indeed, the varnish stratigraphy was formed over successive unknown periods, while the gut strings underwent successive replacements for playing purposes. The approach was extended to varnishes and lacquers on early pieces of furniture and horse-drawn carriages. Beyond deepening our knowledge about dating and provenance on complex undocumented materials, the methodology may contribute to the construction of a history of the use and maintenance or restoration practices of Heritage objects.

2. Perspectives

- ^{14}C dating

The application of ^{14}C dating during this PhD was made possible thanks to a multi-disciplinary framework including restoration, history of technology, material characterization and ^{14}C dating disciplines.

Early varnishes

While early varnishes have been previously studied through historical and physico-chemical approaches, ^{14}C dating adds a new level of information on musical instruments as objects of (musical) use. The ideal approach would be to develop the methodology in close collaboration between restorers and scientists to document varnish stratigraphies which are sampled layer by layer *in-situ* under UV light and optical microscope using microchisels, then analyzed by SEM-EDS and Py-GC-MS and finally appropriately treated for ^{14}C dating. Ideally, to obtain more easily

interpretable results, microsamples would have to be taken during the same sampling mission, although the development of long-term integrative approaches is more suitable in a realistic world. Due to conservative issues, microdestructive analyses are limited for Heritage objects. However, restoration interventions could be opportunities to preserve unrestored areas and store potentially removed (and properly documented) materials, avoiding organic solvents.

Gut strings

In this research, ^{14}C dating on gut strings was studied based on violin making expertise, written sources and patents from the 16th to the 19th c. However, a material characterization approach would also have to be developed to support the interpretation of the ^{14}C results. Material analyses could deepen scientific knowledge on the history of gut strings and the differences between pre-industrial and industrial gut strings, as has already been done for iron piano strings from the early 19th c. (Durier et al., 2019b). Another possible research avenue might be to isolate and date separately residues of colophony from the last period of use of the gut strings. The possible impact of solvents on ^{14}C dating to remove colophony from gut strings must also be further evaluated according to the evaporation efficiency before ^{14}C measurements.

Other parts of musical instruments?

^{14}C dating could be used on other organic parts of musical instruments including violin bows which comprise wood, horse hair, traces of colophony and varnishes. Currently, the dating expertise of bows is based on stylistic relevance with iconographic studies even though several styles continued to coexist after main changes through time (Poidevin, 2009) since dendrochronology cannot be applied on the wood of bows. However, one of the limitations is that ^{14}C results include the duration of material storage, which needs to be discussed from a multi-disciplinary approach.

Bulk varnish and molecular extractions

The dating of “bulk” varnishes provides further information on the impact of inorganic and organic composition on ^{14}C measurements that could be anticipated in future protocol development using adapted chemical pre-treatments for decontamination. The dating of linseed oil/colophony mixtures with 70:30 proportions (as analyzed on Stradivarius violins, Echard, 2010) showed that the main ^{14}C contribution comes from the linseed oil fraction (75%). Fortunately, as this material was used fresh (without a long-term storage period), its ^{14}C dating corresponds to the period of varnish application (whether original, maintenance or restoration). A perspective could be to pursue research on the storage and trading practices of other early organic binders. ^{14}C dating could also be used in future studies to highlight the presence of organic binders with a high impact on ^{14}C measurements but which prove difficult to identify using classical material characterization techniques: for example, binders such as (sub)fossil resins, bituminous products, as well as undetected restoration traces using petroleum-based solvents. The impact of several pigments on ^{14}C dating was assessed during this PhD after applying current dedicated chemical pre-treatments. Other pigments could be investigated in future studies. The effects of the interactions of carbons from linseed oil and driers/pigments could also be explored, as the more we know about the effects of pigments, driers and chemical bonds with organic binders on ^{14}C dating, the more appropriate the chemical pre-treatments will be. To go further, other extraction treatments could be explored such as solid-phase extraction (SPE) or LC-GC in order to avoid derivatization and organic solvents for molecular ^{14}C dating. We note that ^{14}C dating applied on microsamples during this

research is highly sensitive to contamination in comparison with ^{14}C dating applied on archeomaterials with less limited sample size.

- **Sr isotopes**

Colophony and natural resins in violin making

Strontium isotope measurements were already tested once on wood used for instrument making and showed that Sr is present at least at minor level (ppm) (Bernabei, 2020). In my PhD work, I have shown that the strontium content is lower in colophony and measured only at trace level (ppb). But even so, I have also demonstrated that colophony strontium isotopes can be used to trace geographical origin. Besides, as preliminary results, I have also measured an even lower Sr content in linseed oil than in colophony. Thus, our protocols still need to be adapted to measure Sr at the trace and ultra-trace levels observed throughout this PhD. We also estimated that the Sr contribution in linseed oil/colophony varnishes comes mainly from colophony. The current sampling size of a minimum of around 1 g of colophony is still a limit for applications on early linseed oil/colophony varnishes. Currently, a perspective could be to apply Sr isotope measurements on early bow colophony and other raw natural resins used in violin making to study their geographical provenance, combining this information with biomarker studies and written sources. And we are now looking forward to evolutions in isotopic measurement technology that will make it possible to isotopically run an amount of strontium as low as the one we expected to find in sampleable chips of early oil-based varnishes.

Linseed oil/colophony mixtures

The effect of the mixture of linseed oil and colophony with different ratios on Sr content could not be studied during this PhD due to contamination using the initially selected protocols. Currently, the Sr concentration in natural resins is theoretically estimated to be higher than in linseed oil. However, further experiments are needed to properly define the Sr contribution of each organic compound. This approach at isotopic scale may highlight markers in varnishes from different violin workshops and anticipate future technological developments to reach microsample size.

Finally, a request to restorers: in order to preserve the testimony of the material history embedded in the initial materials before restoration interventions, would it be possible to save a few unrestored cm^2 ? They could be taken from the back or inside of the object so as not to impinge on the visual aspect of the object. This would allow future studies to still have access to the original materials, without subsequent contamination.

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Appendix 1. Organic geochemistry investigations

1. Introduction

The purpose of this appendix is to present the preliminary investigations I carried out on linseed oil/colophony mixtures. My intention was to examine the possibility of independently extracting biomarkers from colophony and biomarkers from linseed oil. This work aimed at defining the experimental conditions that would have allowed this separation. As a first step, I adapted the GC procedures to the characterization of the targeted molecules and verified that the extracted compounds were pure (free of contaminants). This work took about three months. I stopped this research when I discovered that the colophony and linseed oil molecules interact strongly, forming a polymeric network after being mixed, cured and dried (Tirat, 2015). It then became impossible to extract individual biomarkers.

The scientific objective of this experimental set-up was twofold: to seek for tree species-specific colophony molecules in a historical varnish in order to obtain a constraint on the potential production area and to directly date these biomarkers by compound specific radiocarbon analysis (CSRA). Unfortunately, these objectives were not met due to the inability to individually extract the proposed biomarkers from the varnish.

2. Brief description of specific molecules

2.1. Colophony

Colophony is a diterpenoid resin containing molecules with a diterpene skeleton ($C_{20}H_{32}$) from two groups of carboxylic acids, abietanes and pimaranes (Figure 117):

- Abietanes: (mostly) abietic, neoabietic and palustritic acids
- Pimaranes: (mostly) pimaric acids, isopiramic and sandaracopimaric acids

The most abundant molecule is dehydroabietic acid (DHA) (Mills and White, 1987; Tirat, 2015).

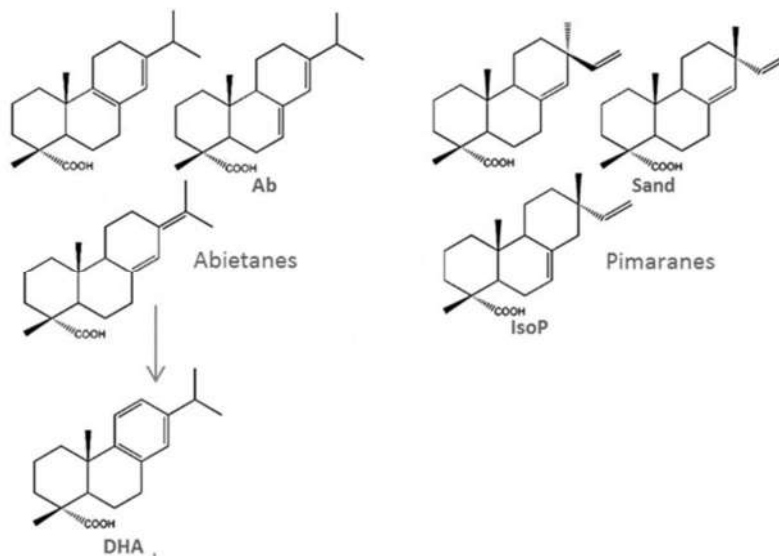


Figure 117. Abietane and pimarane diterpenoic acids, the most abundant molecules in colophony (adapted from Tirat, 2015)

2.2. Linseed oil

Vegetal oils are composed of linear triglycerides (TAGs), glycerol triesters, and fatty acids. TAGs comprise 3 branches of fatty acids linked to a glycerol molecule by ester bonds (Figure 118). Linseed oil contains saturated fatty acids: Stearic acids (S) (C18), Palmitic acids (P) (C16) and unsaturated fatty acids: Oleic acids (O), Linoleic acids (L), Linolenic acids (Ln)(Figure 119). The triglyceride LnLnLn is the most abundant (Wicks et al., 2007). Linseed oil is one of the drying vegetable oils thanks to its high content of unsaturated fatty acids before drying and ageing (Wicks et al., 2007; Échard, 2010).

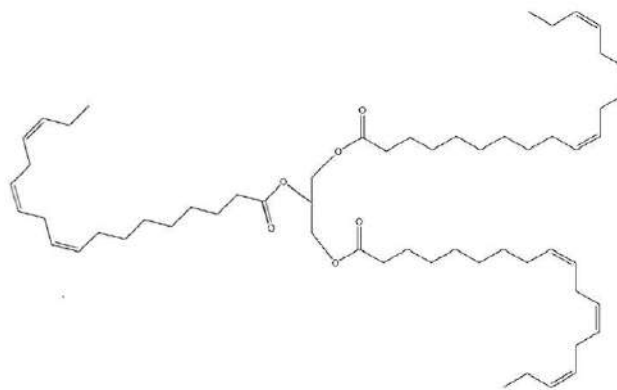


Figure 118. Molecule representation of a triglyceride LnLnLn

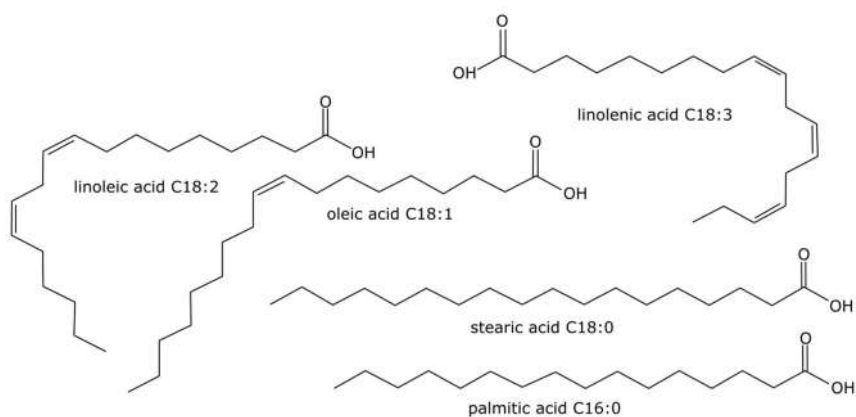


Figure 119. Molecules of saturated and unsaturated acids

2.3. Drying of the linseed oil/colophony varnish

This section presents the interaction between colophony and linseed oil during the preparation and drying stage of the varnish (Figure 120).

Tirat et al. (2017) reported tests on the reconstruction of linseed oil/colophony varnishes with 6 different proportions of the two compounds. 5 different temperatures and 3 curing durations were used to simulate the preparation of early violon varnishes. The siccative effect of colophony was evaluated as well as the rheological behaviour of the mixture and its physico-chemical state using size exclusion chromatography (SEC) at different drying times.

During the curing of varnishes, mechanisms such as dimerization of the drying oil and interactions between the oil and the resin take place (Wicks et al., 2007). There is a formation of ester bonds between triglycerides (TAGs) and polymerization by the carboxylic acid function for diterpenes. (Tirat, 2015) concluded that co-polymerization between linseed oil and colophony occurred, with the formation of an adduct, a hybrid compound with a triglyceride (TAG) and a diterpene molecule (Figure 121). The amount of free diterpenic molecules detected is indeed very low (Tirat, 2015).

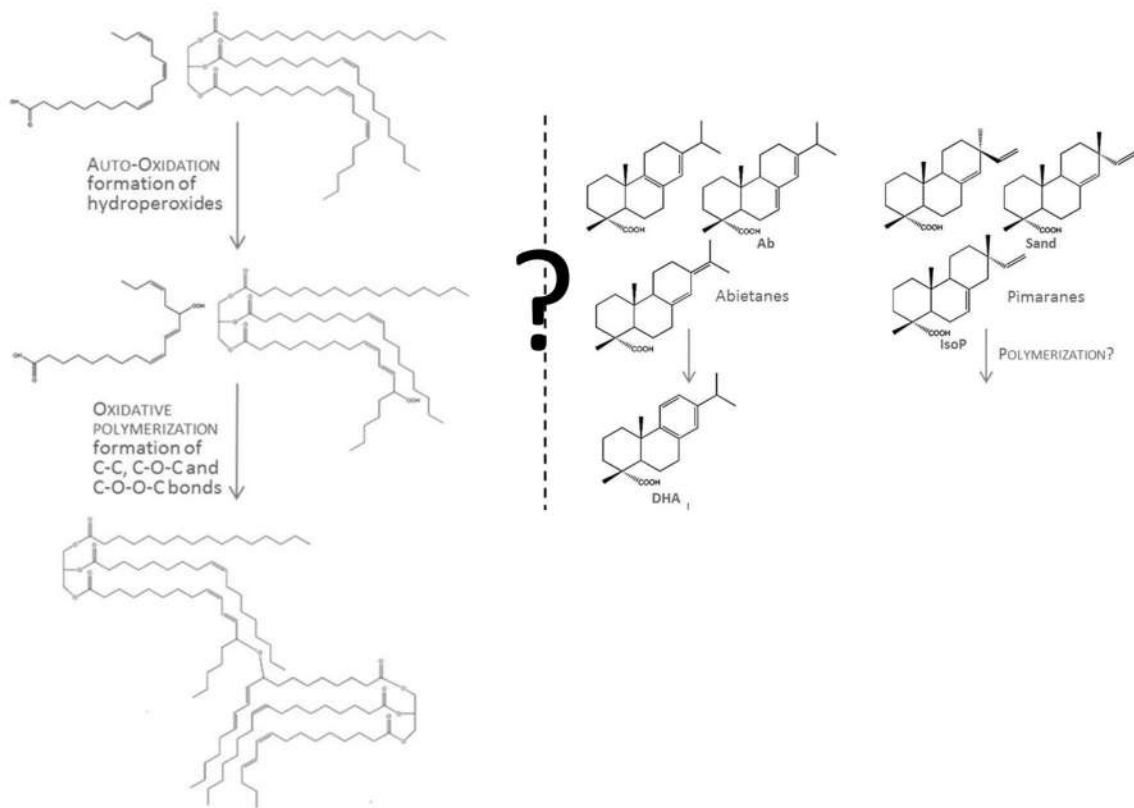


Figure 120. Description of the drying process (adapted from Tirat, 2015)

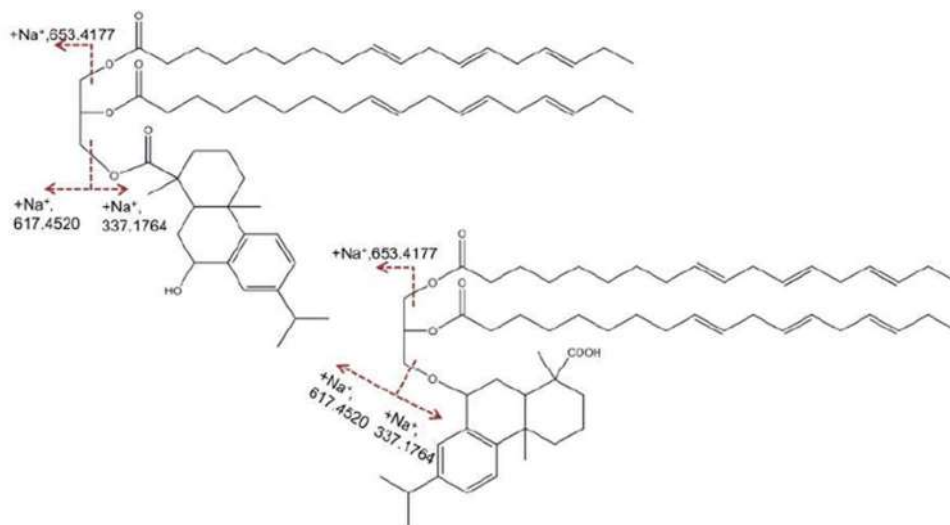


Figure 121. Formation of an adduct between linseed oil and colophony molecules (adapted from Tirat, 2015)

3. Experimental protocol

3.1. Separation

In the literature, the chemical extraction of diterpenes and triglycerides is performed using different types of chromatography and other techniques in the paper industry (tail oil) or in the

food industry fields. Here, we first tested the identification and separation of molecules from linseed oil and colophony according to their chemical properties, followed by quantification of the molecular fractions using GC-MS. ®Old Holland linseed oil and ®Laverdure colophony were used as solvent-soluble materials. ®Old Holland linseed oil is cold pressed windmill linseed oil and is unclarified (avoiding chemical treatments) and the ®Laverdure colophony was produced in the 1980s in the Landes. As a first step, the possibility of using liquid-liquid extraction with methanol-heptane was investigated to separate non-polymerized linseed oil and colophony (Table 43).

Table 43. Solubility tests with some solvents

Solvents	Colophony	Linseed oil
Heptane	No coloured dissolution	Partial dissolution
DCM	Total dissolution	Total dissolution
Acetone	Partial dissolution	Partial dissolution
Methanol	Partial dissolution	No coloured dissolution

Molecular fractions of ®Old Holland linseed oil and ®Laverdure colophony were separated according to their polarity using columns of dry silica with different eluents. Geosh protocols were used to separate the molecules according to increasing polarity into 5 fractions (cyclohexanes, alcohols, alkenes, aromatic molecules, etc.) (Figure 122). Prior to molecular identification and quantification using GC-MS, molecular fractions with chemical functions such as terpene acids, ketones, etc. have to be derivatized (e.g. silylation).



Figure 122. Application of the Geosh protocols to separate molecular fractions according to increasing polarity (cyclohexanes, alcohols, alkenes, aromatic molecules, etc.).

3.2. Identification and quantification of molecules

After separation and derivatization (esterification or silylation), the molecules were identified and their fractions were quantified. The derivatization of molecules for GC-MS analyses induces ¹⁴C contamination. A solution could have been to implement a calculation of error propagation;

however, a more suitable solution is to avoid derivatisation steps. We therefore quantified the neutral fractions in linseed oil and colophony.

3.2.1. GC protocol

The initial experimental program was adapted to the specificities of the chemistry laboratory at LSCE-GeoTrAc in order to handle the linseed oil/colophony samples. The feasibility study was based on the strategy of using the Prep-GC FC present in the laboratory to separate, purify and collect molecular fractions which were then dated using the ECHoMICADAS AMS.

The conditions for GC-MS at LSCE are as follows: through an AS 3000 (TMThermoScientific) sample changer, solvent extract (1 μ L) was injected into an injector with an on column adaptor connected to a SGE (Analytical Science) BPX5 column (12 m \times 0.22 mm \times 0.1 μ m). Helium was used as the carrier gas (1.2mL/min.). The Trace 1300 (TMThermoScientific) Gas Chromatograph is coupled to a ISQ QD (TMThermoScientific) Mass Spectrometer. Separation was conducted using a GC oven temperature program consisting of:

initial temperature, T ₀ :	80 °C
ramp 1:	30 °C/min
T ₁ :	120 °C
ramp 2:	40 °C/min
T ₂ :	310 °C
temperature plateau:	310°C for 40min

Spectra were obtained in full scan mode after 1h30 (m/z 50 to 650).

3.2.2. Colophony

Colophony mainly comprises acids that require derivatization prior to elution (Figure 123). The separation of the neutral fraction corresponds to the molecules that do not need derivatization. Around 0.1 μ g of neutral molecules per 100 μ g of colophony from [®]Laverdure were quantified after GC-MS analyses performed at the LSCE laboratory (Table 44).

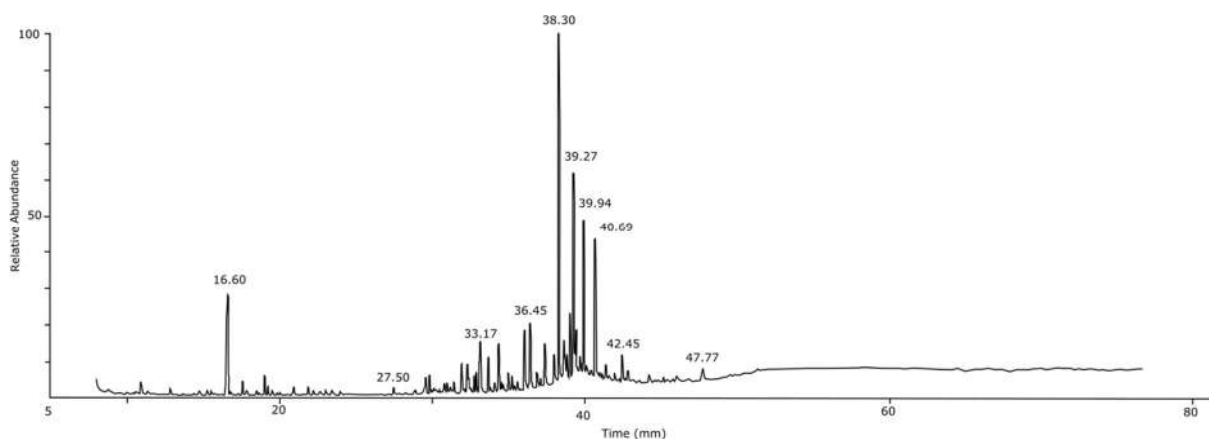


Figure 123. Chromatogram of the total fraction of molecules in a colophony from Laverdure 1998

Table 44. Concentration of the neutral molecule fraction in Laverdure 1998 colophony - ug/g (or ppm) and identification of some molecules in the neutral fractions F3, F4/5, F6/7

F1- Aliphatic and cyclic hydrocarbons	F2 - Aromatic hydrocarbons	F3 - Ethers	F4/5 - Ketones/alkenones	F6/7 - Alcohols/sterols/Triterpenols	Total Neutral fraction of unsilylated molecules
666.77	111.16	482.86	3102.62	3701.73	1260.79
Rumuen	Cadalene				
Kaurene	Cadinene				
Pimaradiene	Cubebene				
Phenanthrene	Rutene				
Labdiene, ...	Norabietatriene, ...				
Isopimara, ...					

3.2.3. Linseed oil

Ester bonds with the glycerol molecule of triglycerides (TAGs) are cut during the analyses and silylated fatty acid chains were detected using GC-MS analyses (Table 45). A chromatogram of the total fraction of molecules in a linseed oil [®]Old Holland is presented in Figure 124.

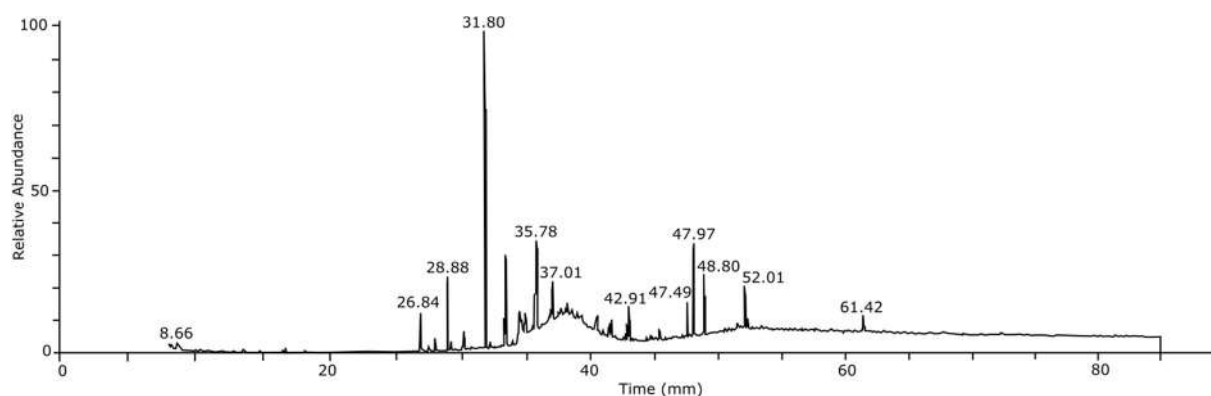


Figure 124. Chromatogram of the total fraction of molecules in a linseed oil from Sennelier 2019 – Old Holland

Table 45. Chromatogram of the total fraction of molecules in an Old Holland linseed oil

Total silylated fraction	Esterified acid fraction	Neutral fraction
octadecanoic acid	Palmitic acid, methyl ester	Neophytadiene, ...
linoleic acid	Octadecanoic acid, methyl ester	
alpha-sitosterol	Linolenic acid, methyl ester, ...	
Linolenic acid		
Palmitic acid, ...		

4. Conclusion

The application of CSRA to separately date the oil and resin binders in the varnishes should theoretically have allowed us to validate or invalidate their contemporaneity and reveal the storage practices in earlier violin workshops as assumed based on written sources. Likewise, the characterization of biomarkers from colophony should have provided clues to the tree species involved in resin manufacture and thus to potential historical production centres.

However, the feasibility tests using chemical preparation and GC-MS analyses at the LSCE highlighted numerous unresolved issues and obstacles.

5. References

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Appendix 2. Equipment description

This research was made possible thanks to the expertise of museum professionals (curators, restorers), scientists in material sciences and specialists of ^{14}C geochronology and geochemistry at the LSCE using proven protocols and equipment run by technicians.

I present here the equipment with its experimental conditions and my degree of autonomy on each analytical step:

Theoretical training	Short practical training	Practical training	Autonomy after update training	Complete autonomy
●○○○○	●●○○○	●●●○○	●●●●○	●●●●●

1. Equipment for material characterization

1.1. *In situ* VIS/IR/UV imaging

Degree of autonomy: ●●●●●

Varnishes were observed *in situ* using VIS/IR/UV imaging before micro-sampling. The equipment described here belongs to the Laboratoire du Musée de la musique.

A Dino-Lite digital microscope with DinoCapture 2.0 software was used to take pictures *in situ* under visible (VIS), IR and UV light. Micro-sampling was performed under UV light using torches (Lumitorch UVLed Pro 30 lumens or NightSearcher UV light 365 nm, 6W). When the equipment was available, micro-sampling was performed under a binocular microscope (Wild Heerbrugg) equipped with an Intralux 5000-1 light system. Otherwise, magnifying glasses were used.

Echard (2010) reported the methodology used at the Musée de la musique to take a general UV picture of musical instruments with a neon tube (F8T5BLB, Magnetek, 365 nm, 8 W) placed at a distance of 15-60 cm from the area that was photographed with a Powershot A95 (Canon) equipped with a yellow filter (2E, Kodak). General digital pictures were also taken under a homogeneous white light LED Lamp (Tiro-Clas or Waldmann).

1.2. Optical microscopy

Degree of autonomy: ●●●●●

Varnish micro-samples were studied for stratigraphic observations under a Zeiss Axio Scope.A1 Vario light microscope in the Laboratoire du Musée de la musique. The Zeiss Axio Scope.A1 Vario system is equipped with Epiplan objectives (5x, 10x, 20x, 50x), a polarizer and a rotating analyzer. Images were acquired using a Leica DFC 320 camera. A Leica DMS1000 optical microscope was also occasionally used at the LSCE. Exceptionally, lacquer samples from the D.04224 Chinese zither were also observed at the Laboratoire des Monuments Historiques under a digital microscope (3D Keyence-VHX) (Durier et al., 2021).

1.3. XRF spectrometry

Degree of autonomy: ●●●●●

An ArtTax⁵⁷ energy dispersive X-ray fluorescence spectrometer (XRF) (Intax GmbH) can be used *in situ* or on micro-samples at the Laboratoire du Musée de la musique. The ArtTax is equipped with a molybdenum anticathode tube and a Peltier-cooled Silicon Drift X-Flash detector from Röntec. The X-ray tube operates at 45kV and 600 μ A. The target was placed horizontally at a working distance of 5 to 6 mm. The spectra acquisition time was 400 s (Echard, 2010).

An X-ray fluorescence spectrometer (XRF) Jetstream M6 from Bruker was also available. The spectrometer is fitted with a rhodium anode in the X-ray tube at 50 kV and 200 μ A with a 100 μ m-thick beryllium window. The beam diameter was 450 μ m. The target was placed horizontally at a working distance of 2 mm. The spectra recording time was 200 s with a maximum count rate of 96 kcps. Data were processed with the Esprit software developed by Bruker (Radepon et al., 2020).

1.4. FTIR-ATR spectrometry

Degree of autonomy: ●●●●○

Fourier Transform InfraRed spectroscopy (FTIR) was conducted with a Nicolet 6700 spectrometer equipped with a diamond ATR module (SMART endurance) and with the OMNIC[®] software (Thermo Fisher Scientific). The equipment is available at the laboratoire du Centre de Recherche sur la Conservation⁵⁸. Measurements were carried out with 64 scans accumulation and a spectral resolution of 4 cm^{-1} . The spectral range was from 500 cm^{-1} to 4000 cm^{-1} .

1.5. SEM-EDS

Degree of autonomy: ●●●○○

Analyses on lacquer samples from the Chinese zither D.04224 were carried out by Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM–EDS) using a JEOL-JSM IT 300 instrument (mode 'HighVacuum', WD=10 mm, an energy beam of 20 keV, mode BED-C) with an X-ray microanalyzer X-MaxN (Oxford) and with Aztec software (Oxford) at the Laboratoire des Monuments Historiques. The sample was previously embedded in a polyester resin ESCIL-SODY 33 and pre-polished with SiC papers to obtain a transversal stratigraphic section (Durier et al., 2021).

1.6. Raman spectrometry

Degree of autonomy: ●●●●○

The following two Raman instruments equipped with an optical microscope (confocal mode, focus \times 50) were used punctually at the Laboratoire des Monuments Historiques⁵⁹: i- the confocal Raman microspectrophotometer INVIA Renishaw with a laser source of 532 nm, ii- the Raman microspectrophotometer with a laser source of 785 nm from BWTek.

⁵⁷ Sylvie Gomes, internship report, 2013, unpublished, available at the Musée de la musique

⁵⁸ Measurements carried out under the supervision of Oulfa Belhadj, Centre de Recherche sur la Conservation

⁵⁹ Analyses performed by Didier Brissaud

1.7. GC-MS spectrometry

Degree of autonomy: ●●●●○

At the LSCE, the Trace 1300 (TMThermoScientific) gas chromatograph is coupled to an ISQ QD (TMThermoScientific) mass spectrometer (GC-MS)⁶⁰ with an AS 3000 (TMThermoScientific) sample changer and a SGE (Analytical Science) BPX5 column (12 m × 0.22 mm × 0.1μm). Spectra were obtained in full scan mode after 1h30 (m/z 50 to 650).

2. Equipment for ¹⁴C dating

The different steps for ¹⁴C dating are described in Figure 125. The samples were first cleaned with mechanical and chemical treatments, then transformed into “pure” CO₂ gas and graphite C before ¹⁴C dating using ECHO MICADAS.

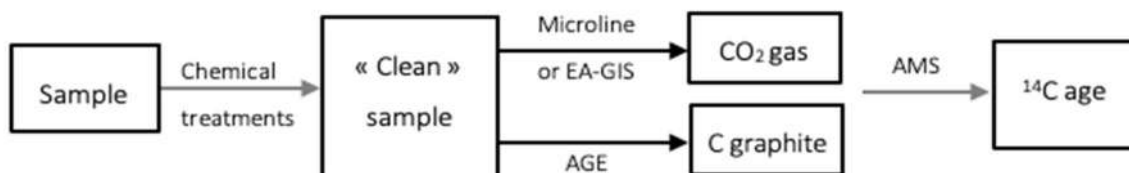


Figure 125. Scheme of ¹⁴C dating using AMS

2.1. Freeze-dryer

Degree of autonomy: ●●●○○

The freeze-dryer transforms the solvents and chemicals used to clean the samples into a solid state by freezing. Finally, ice sublimation removes the solvent and chemical traces. This principle is also known as freeze-drying and the different steps are based on modifications in the pressure and temperature parameters (Figure 126).

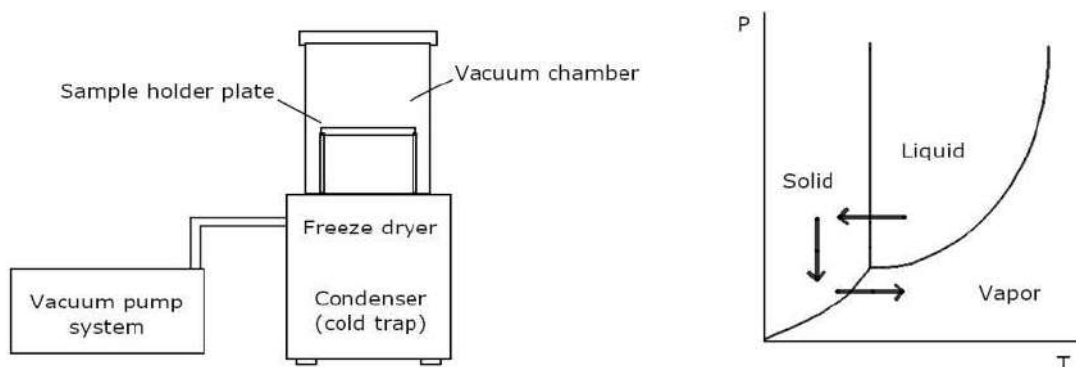


Figure 126. Scheme of the lyophilization principle

⁶⁰ Analyses performed under the supervision of Jérémy Jacob, LSCE.

2.2. Microline

Degree of autonomy: ●●●●○

Experimental objective:

The microline is used for both the combustion of small-sized organic samples (less than 400 μ gC) and unknown carbon content and for the thermal decomposition of white lead. If possible, the target is to get 2 tubes of CO₂ of 100 μ gC each. The line allows the conversion of samples into CO₂ and the purification and quantification of evolved CO₂.

The transformation into "pure" CO₂ is carried out on "clean" samples after chemical treatments (Figure 125). The microline consists of a hermetic system of glass tubes and operates under vacuum with a pressure of about 10⁻⁶ mbar. The protocol has been optimized at the LSCE to reduce the risk of contamination by actual atmospheric CO₂ and the risk of isotopic fractionation (which would induce final ¹⁴C/C and ¹³C/C ratios different from the initial ratio of the sample) (Pham, 2007).

Experimental installation

The microline system is divided into 4 parts: i- a pumping system to create a vacuum, ii- a part for sample combustion, iii- a part for gas transfer and purification, iv- a part for gas conditioning.

- Pumping system

Two pumps are connected in series, the primary and secondary pumps. The primary pump creates a first vacuum of 10⁻² bar (valves A2 and then A3 are closed, and A1 is opened, Figure 127) and then, the secondary pump produces the required vacuum of 10⁻⁶ bar (valve A1 is closed, then A2 and A3 are opened, the primary pump is still running, Figure 127). All the line is kept under 10⁻⁶bar vacuum. This includes the sample in the quartz sample tube if there is no risk of sublimation. In the case of potential sublimation (e.g. phthalic acid, oxalic acid), a low vacuum (depending on the sublimation pressure, typically $\sim 10^{-1}$ bar) will be used just before combustion.

- Combustion of organic samples

This step was carried out either with a flame combustion using O₂ in the sample glass tube or with an oven. For samples with no risk of sublimation, the O₂ is introduced from the pure O₂ cylinder to the evacuated quartz sample tube, at a typical pressure of ~ 0.15 atm. In the case of potential sublimation, a low vacuum is applied to the sample just before combustion. O₂ is then introduced and pumped at low pressure, then re-introduced and pumped. This cycle is performed at least 3 times to replace air molecules by O₂ without any risk of sample loss by sublimation.

When used, the tubular oven (open on both sides) is placed around the quartz sample tube, 3 to 5 cm above the sample. The temperature of the oven then rises to 920°C. The oven is then moved from the top to the bottom at a rate of ~ 3 min per centimeter. This allows a complete oxidation of the sample, including the oxidation of light molecules that evaporate at temperatures below 920°C but that meet the 920°C zone under gaseous forms and are fully oxidized there into CO₂.

- Thermal decomposition of white lead

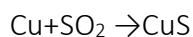
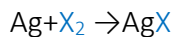
No O₂ is introduced to thermally decompose white lead. The decomposition is performed with the tubular oven moving from top to bottom. Beck et al. (2019) recommended a temperature of 400°C. This value was reassessed by Messenger (2020) who recommended 300°C.

- Gas transfer with CO₂ purification and extraction

Gas transfer follows a series of cryogenic traps and ovens based on the natural movement of gas from the hot point to the cold point.

After combustion of the sample, evolved gases pass through oven 1 which contains glass beads maintained at 200°C. This is to increase the contact time between evolved gases and O₂ to further increase the oxidation efficiency of nitrogen compounds since the most oxidized forms show the highest solidification temperature. They are therefore more prone to be trapped in the cryogenic trap maintained at -78°C (dry ice and alcohol), that completes this part of the line. The remaining evolved gases are then trapped in liquid nitrogen (T=-196°C). The untrapped gases, including O₂ excess, are pumped out.

The gas then passes through oven 2 at 450°C which contains Ag and Cu, removing halogens (X₂) and traces of O₂ and SO₂:



After another cryogenic H₂O trap and CO₂ trap, the CO₂ gas pressure is measured on a calibrated cold finger. The amount of carbon is then evaluated (J2, Figure 127). Finally, the purified CO₂ gas is flame-sealed in one, two or three Pyrex tubes (Figure 128).

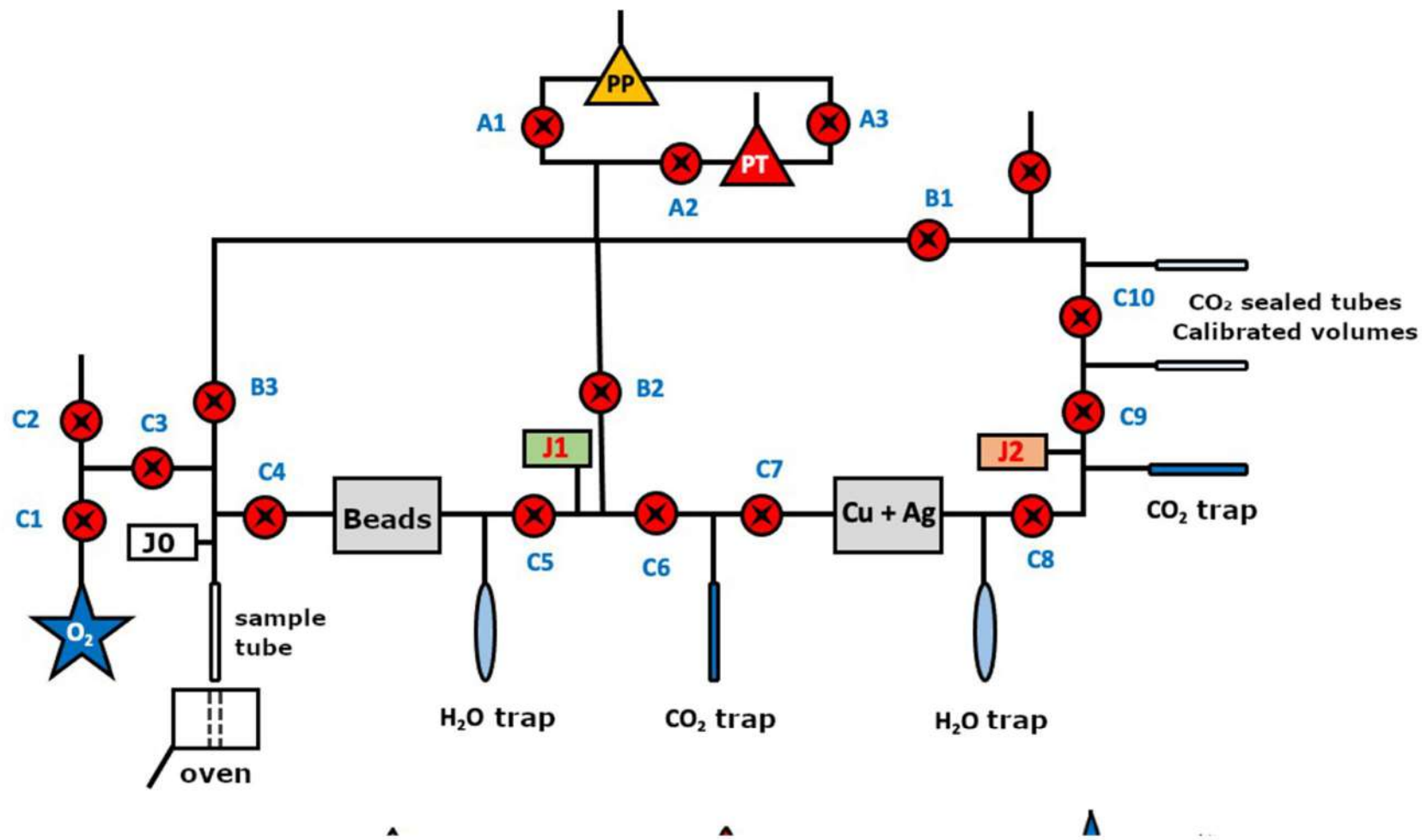


Figure 127. Scheme of the principle of use of the microline

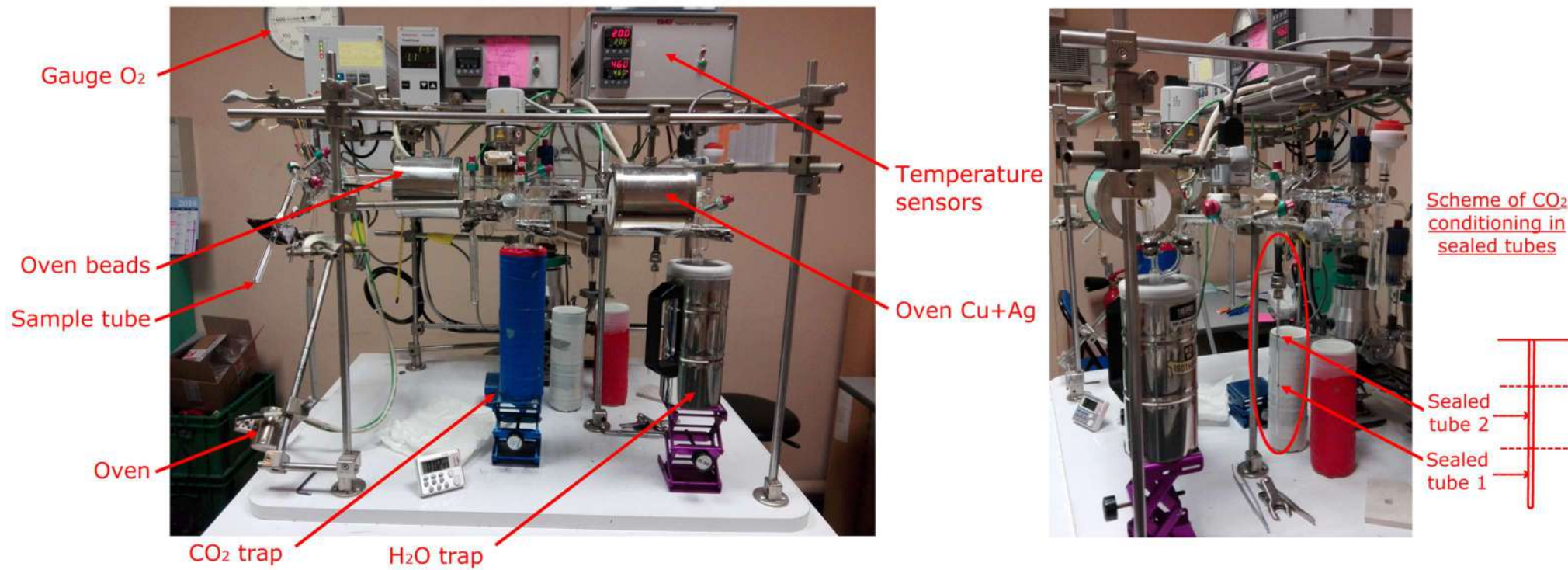


Figure 128. Pictures of the microline for extraction and purification of CO₂

2.3. Automated Graphitization Equipment (AGE3)

Degree of autonomy: ●○○○○

Experimental objective:

At LSCE, the Automated Graphitization Equipment (AGE3) is coupled to an Elementary Analyzer (EA). This combination allows the combustion of organic samples at high temperature in the presence of oxygen, the purification of CO₂ and its reduction to carbon graphite in the presence of H₂ and iron as catalyst and support. The LSCE equipment was developed by ETH Zürich (Wacker et al., 2010) and today's equivalents are sold by Ion Plus. At LSCE, it is typically used for samples containing at least 400 µg of carbon.

Samples wrapped in tin caps are introduced in the sample changer to be burned in an elemental analyzer (EA). The CO₂ gas is absorbed in a zeolite trap and then released by heating. The CO₂ gas is graphitized through the following reduction reactions with iron powder (Fe) as catalyst, while water is trapped during the graphitization reaction to avoid reversibility (Figure 129):

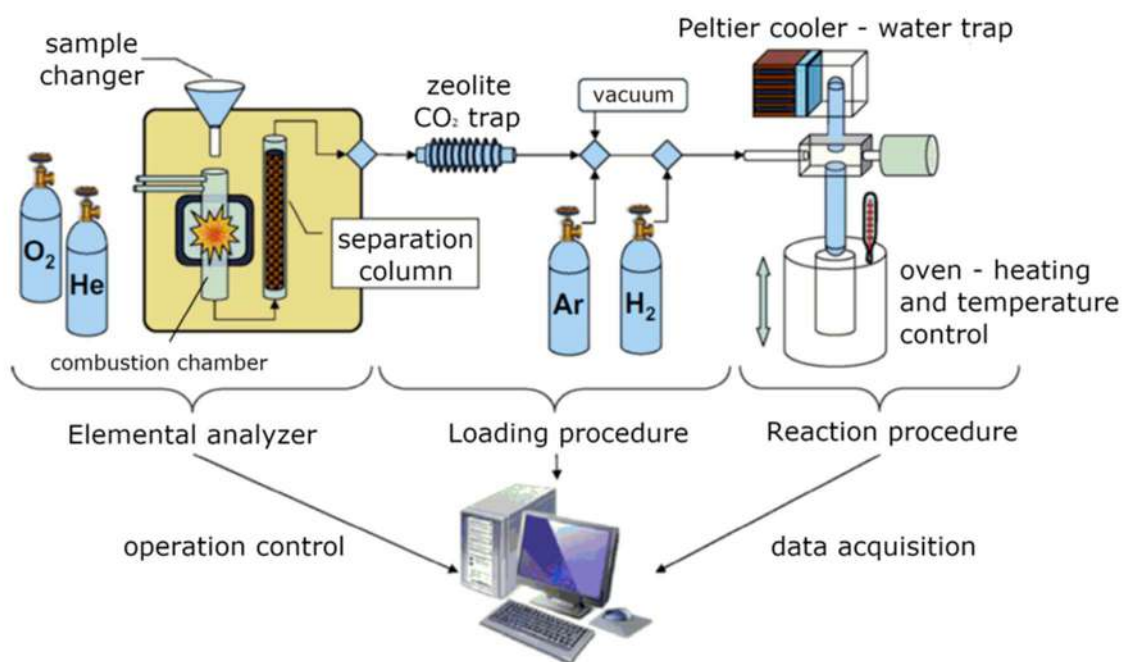
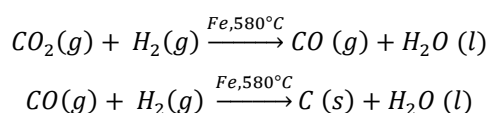


Figure 129. Simplified operational scheme of the graphitization line (Ionplus)

2.4. GIS system

Experimental objective:

The gas interface system (GIS) developed by ETH Zürich (Ruff et al., 2007) and now sold by Ion Plus is used for direct ¹⁴C measurement on samples with a carbon content of about 10-100 µg. The CO₂ gas is mixed with helium gas continuously injected into the ion source of ECHOMICADAS. Two options are possible (Figure 130):

- i- Samples wrapped in tin caps are combusted in an elemental analyzer coupled with the GIS system (EA-GIS – Ruff et al., 2007). The CO₂ gas is absorbed in an integrated zeolite trap, then released by heating into the syringe to be fed into the ion source.
- ii- CO₂ samples sealed in glass tubes after extraction using the microline can be introduced in tube crackers of the GIS system, then the gas is released into a syringe and introduced into the ion source.

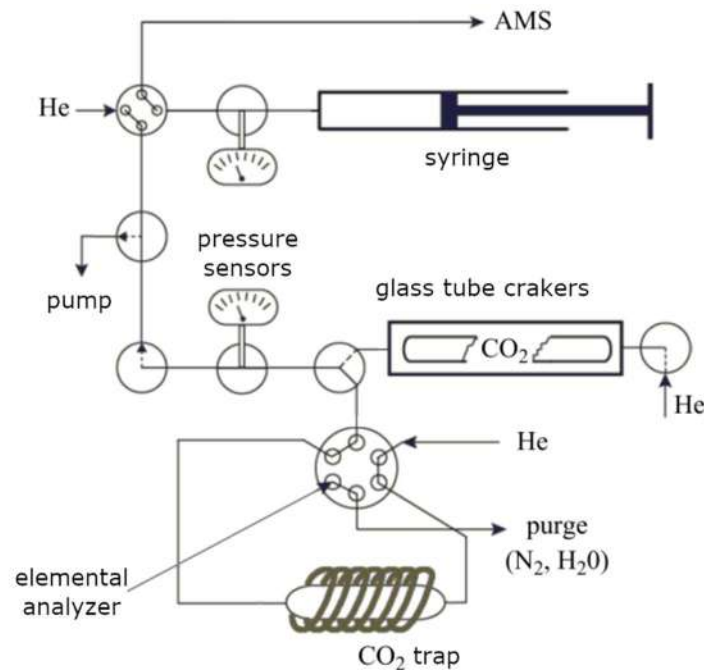


Figure 130. Introduction system of CO₂ samples in the AMS ion source (Ionplus)

2.5. ECHOMICADAS AMS

Degree of autonomy: ●●○○○

The ECHOMICADAS (Environnement, Climat, Homme Mini ¹⁴C ARbon DAting System) consists of a particle accelerator coupled with mass spectrometers (AMS) dedicated to the detection of the natural carbon isotopes ¹²C, ¹³C and ¹⁴C. The natural abundance of the radioactive isotope ¹⁴C is very low compared to the stable carbon isotopes (10⁻¹⁰ atoms of ¹⁴C, 1 atom of ¹³C and 99 atoms of ¹²C for a total of 100 atoms). Samples are introduced into the ECHOMICADAS AMS as graphite or CO₂ gas. The equipment comprises: i- an ion source, ii- a low energy mass spectrometer, iii- a particle accelerator, iv- a high energy mass spectrometer, v- Faraday cups, vi- a gas ionization chamber (Figure 131).

- i- the sample is targeted with cesium (Cs⁺) in the ion source, then the gas is negatively ionized,
- ii- the negative C⁻ ion beam is accelerated and passed through a low magnetic field mass spectrometer: ¹²C and ¹³C are light and are deviated from the central beam in Faraday cups, whereas ions with m/z=14 are selected (¹³CH⁻, ¹²CH₂⁻, ¹⁴C⁻),
- iii- the negatively charged gas becomes a positively charged gas through a particle accelerator with helium gas flow (¹²C⁺, ¹³C⁺, ¹⁴C⁺),

- iv- the positive C^+ ion beam is accelerated and passed through a high energy mass spectrometer,
- iii- trapping and counting of ^{12}C and ^{13}C in Faraday cups,
- iv- detection of ^{14}C in an ionization chamber

Sample series are measured with alternating sequences of phthalic acid (blank) and oxalic acid (standard) to correct measurements including isotopic fractionation effects.

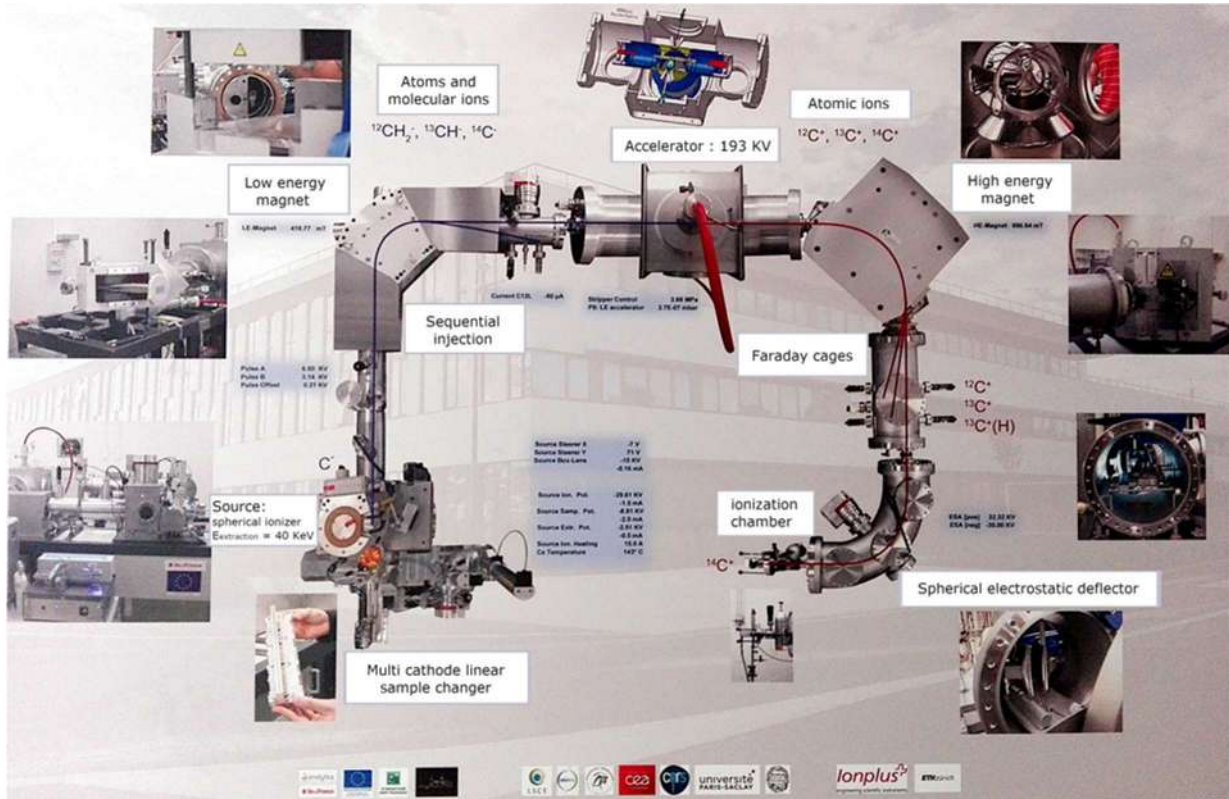


Figure 131. Descriptive scheme of the AMS ECHoMICADAS (LSCE)

3. Equipment for Sr isotope measurements

3.1. Clean room

Degree of autonomy: ●●●●○

The Sr element is extracted and purified in a clean lab before concentration and isotope measurements using digestion and ion chromatographic procedures (Figure 132).

Samples, taken up in a 3 M HNO_3 solution, are loaded onto pre-cleaned Sr-Spec cation exchange resin columns (Eichrome Inc.). Sr is eluted in 2.5 mL ultrapure Milli-Q. Samples resulting from the chemical separation are dissolved in nitric acid (0.5 N HNO_3) before being injected, at an adjusted Sr concentration, into the ICP-MS source.

The chemical step helps to reduce interferences and matrix effects. There are two kinds of interferences: i- isobaric interferences i.e. ions and/or isotopes from different elements sharing

a common mass, ii- molecular interferences i.e. ionized molecules of isotopes sharing a common mass, especially with atoms from the air or argon flow (e.g. $^{40}\text{Ar}^{16}\text{O}^+$ and $^{56}\text{Fe}^+$).

Matrix effects induce sensitive changes such as mass bias which can be reduced by measuring samples and standards with the same matrix. We thus measured soil samples separately from pine resin samples.

Collision/reaction cells added to the ICP-MS and MC-ICP-MS equipment can reduce molecular interferences by interactions with a gas such as helium.

N° Elution	1	2	...	16	BLC chimie	STD
mise de la resine dans les colonnes			...			
lavage résine: 3*HNO ₃ 3N, 3* MilliQ			...			
Prélèvement traces, et pré analyses 0,5mL			...			
charger ech en 4*1mL			...			
Rinçage du calcium 3* 1ml HNO ₃ 3N			...			
Placer tubes 5mL et Elution du Sr, en 5*0,5mL de MilliQ			...			

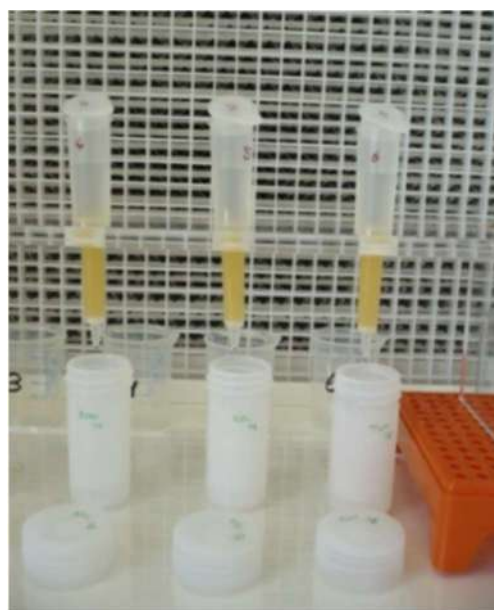


Figure 132. (from left to right) Sample tracking form to be filled by the lab technician and picture during elution onto cation exchange columns charged with pre-cleaned Sr-Spec (Eichrome Inc.) resin

3.2. ICP-MS

Degree of autonomy: ●○○○○

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is used for multi-element measurements at major, minor and trace levels.

Sr concentrations were measured at the LSCE using an Inductively Coupled Plasma-Quadrupolar Mass Spectrometry X-SeriesII (ICP-QMS, Thermo Scientific™). The equipment comprises (Figure 133):

- i- a sample introduction system: the liquid sample is injected into a nebulizer coupled with an argon plasma torch (around 8000°K). The aerosol is atomized and ionized under high energy, then sent through a cone interface for ion extraction,

- ii- an analyzer system: the ions pass through a quadrupolar system with separation according to the m/z ratio using linear voltage variation,
- iii- ion detection system (Faraday cups, electron multipliers).

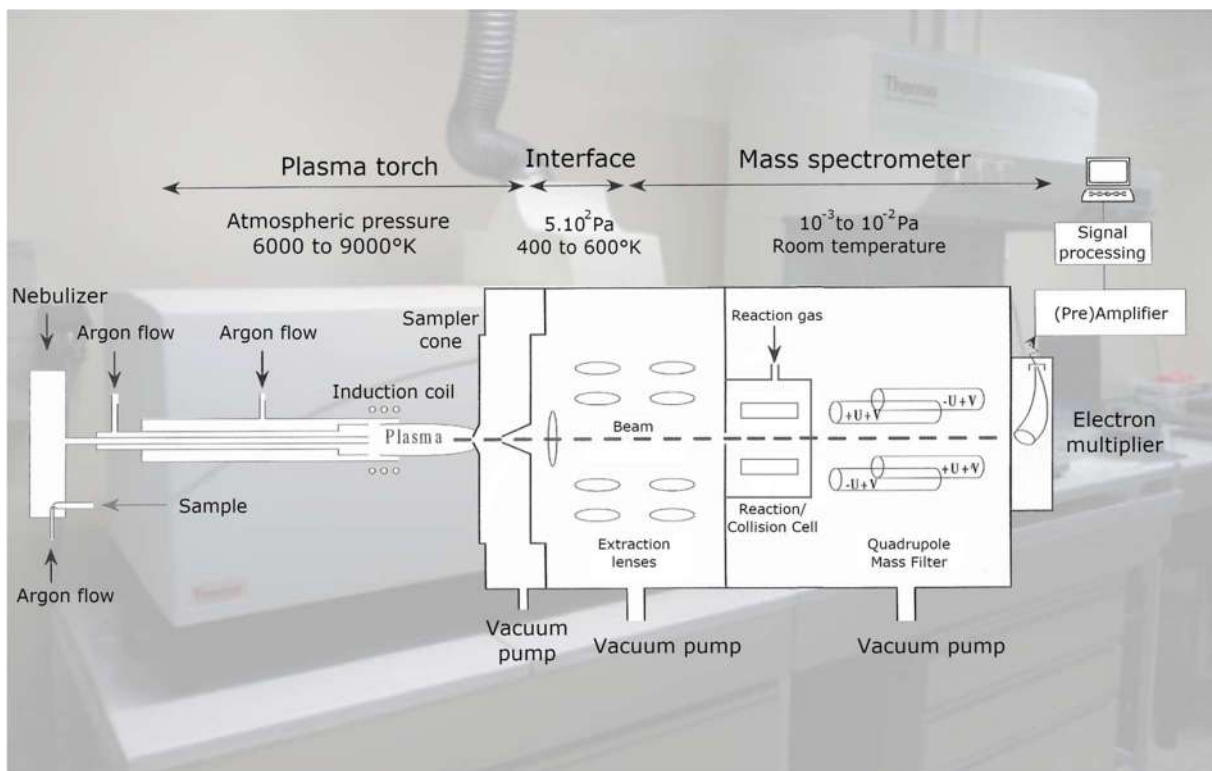


Figure 133. Scheme of the principle of quadrupole ICP-MS

3.3. NEPTUNE MC-ICP-MS

Degree of autonomy: ●○○○○

Multi-Collector Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS) is dedicated to isotope measurements possibly for more than 40 elements. The sample can be introduced as a liquid, as an aerosol, or optionally as a solid if the introduction interface is coupled with a laser ablation system. The ionization efficiency is high for most elements (>90%) using the plasma source.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured at the LSCE using a Neptune^{Plus} MC-ICP-MS (Thermo Scientific™). The equipment comprises (Figure 134):

- iv- a sample introduction system: the liquid sample is injected into a nebulizer coupled with an argon plasma torch. The aerosol is atomized and ionized under high energy, then sent through a cone interface for ion extraction;
- v- an analyzer system: the ion energy dispersion is corrected with a double-focusing system to form an ion beam and optimize its trajectory until reaching the detectors. The ions pass through the electrostatic sector and the magnetic sector with separation according to the m/z ratio;

- vi- multi-collector and detector array for simultaneously measurements of multiple isotopes (Faraday cups, electron multipliers) with a high signal stability, sensitivity and reproducibility.

A bracketing system is used to correct machine drift: “standard-blank-sample-blank-standard, etc.” The reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was evaluated compared to the NBS 987 standard value of 0.710245.

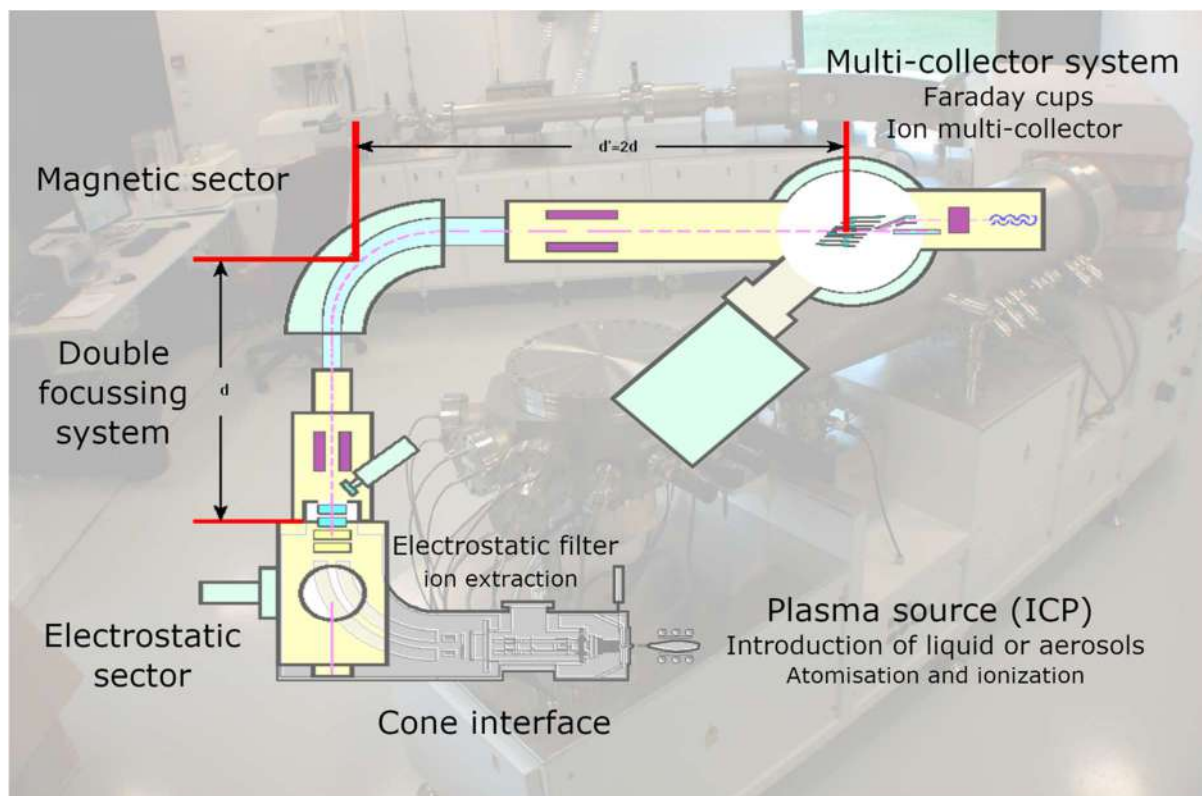


Figure 134. Scheme of the principle of MC-ICP-MS

4. References

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Appendix 3. Samples for ^{14}C dating

1. Prospection corpus for ^{14}C dating

This table lists the non-exhaustive prospection carried out to collect a material corpus for the application and calibration of ^{14}C dating measurements, mainly on early oil-based varnishes from the modern period. The main contacts are presented here. Some contacts could not be solicited due to lack of time between the end of my first year of PhD dedicated to bibliographical research (December 2019) and the beginning of lockdown due to the Covid pandemic (March 2020), for example:

Jean-Jacques Rempal, Nicolas Perrin, Jean François Raffin, Association la Ménestrandie, Claudio Canevari; Colin Irving, luthier in Somerset, England; EILA; Harvard's Fogg Museum; Mimi Waitzman at the Horniman Museum; Harvard's Fogg Museum; Ringve Music Museum; The Bate collection, Oxford; Maestronet forums; ACC Art Collection Care; etc.

Legend in the table of sampling prospection for ^{14}C dating application

- [1] Partnership: sample collected
- [2] Ex-partnership: sample collected and no further information exchange
- [3] Potentially qualified: possible samples of interest with required agreement
- [4] Network: a contact providing new contacts
- [5] Out: no positive reply and no further information exchange



collected samples






samples of interest not collected




sampling refusal or unsuitable samples

Table 46. Recapitulative table of sample prospection

request	Name	Contact	State	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10	
Early oil-based varnishes for ¹⁴ C dating	Louvre Département des Objets d'art du Moyen-Age, de la Renaissance et des temps modernes	Frédéric Dassas	Partnership [1]	12/12/2019 -> Email	17/12/2019 -> Email - information request	18/12/2019 -> Emails/Phone calls	19/12/2019 -> Meeting with Frédéric Dassas	06/01/2020 -> Email + Phone call - Reminder	07/01/2020 -> Email – Meeting schedule	10/02/2020 -> Email - presentation of the PhD project	11/02/2020 -> Meeting - presentation of the PhD project	11/05/2020 -> Email - New contact after the Covid-19 lockdown to reschedule the sampling mission	11/05/2020 -> Email - Schedule of the sampling mission 28/07/2020	
	KMKG-MRAH	Emile Van Binnebeke		30/01/2020 -> Email	10/02/2020 -> Email request	18/02/2020 -> Phone call	21/02/2020 -> Phone call	21/02/2020 -> Positive reply by email	02/03/2020 -> Email – Meeting schedule	09/03/2020 -> Meeting schedule 30/03-03/04/2020	16/03/2020 -> mission postponed due to Covid pandemic	17/07/2020 -> visio-conference	25/08-28/08/2020 -> sampling mission	
	Musée de la lutherie et de l'archèterie françaises	Valérie Klein		18/12/2019 -> Email	12/01/2020 - 15/01/2020 -> Stéphane Vaiedelich's mission at Mirecourt	02/03/2020 -> Agreement for sampling - postponed due to coronavirus	03/04/2020 -> On-going partnership	14/04/2021 -> sampling mission at the Musée de la musique	03/05/2021 -> sampling mission at the Musée de Mirecourt	04/05/2021 -> sampling mission at the Musée de Mirecourt				
	Musée National de la Voiture et du Tourisme, Compiègne	Richard Keller Maria-Anne Privat		12/02/2020 -> Email contact with Richard Keller via Kristelle Besson	17/02/2020 -> Email - Information request for varnish sampling	25/02/2020 -> Phone call	16/03/2020 -> postponement of the sampling mission due to the Coronavirus	12/05/2020 -> Phone call	28/05/2020 -> visio-conference - project presentation	08/06/2020 -> email – sampling project report	07/07/2020 -> Phone call for sampling mission schedule	04/08/2020 -> Sampling mission at the Musée de Compiègne	06/08 - 07/08/2020 -> Sampling at the Musée de Compiègne	
	Atelier Perrin	Nicolas Perrin		11/09/2019 -> Phone call	17/10/2019 -> Appointment schedule	28/11/2019 -> Appointment at the workshop	4/12/2019 -> Email reminder (Cello Jean-Theodore Namy, Paris, 1773; Cello head, 18 th c.)	12/02/2020 -> email to delay the sampling due to methodological issues	24/06/2020 -> sampling of the cellos at the Musée de la musique					

request	Name	Contact	State	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10
Early oil-based varnishes for ¹⁴ C dating	Fairfax Violins	Andrew Fairfax	Potentially qualified [3]	17/12/2019 -> Email	31/01/2020 -> Email	07/02/2020 -> Reply email	02/03/2020 -> sending of a sample of Venetian varnish c.1700 - Montagnana cello - restoration in the workshops of WE Hill & Sons						
	Centre de restauration des biens meubles de Catalogne (CRBMC)	Ricardo Suarez		20/01/2010 -> Email contact via Victoria Beltran	28/01/2020 -> reply email with object list	28/01/2020 -> reply email with object list	15/03/2020 -> contact ended due to the Covid pandemic						
	Andrew Hooker Violins	Andrew Hooker		17/12/2019 -> Emails	9/01/2020 -> reply email (Violon, Claude Pierray, c.1720, Paris, Violon, Jacques Bocquay, c.1720, Paris)	20/01/2020 -> Email	28/01/2020 -> Email - Skype appointment	03/02/2020 -> too much contamination by later polishing and adding on the varnishes of the 2 violins.					

Early oil-based varnishes for ¹⁴ C dating	Augerson Art Conservation Services	Christopher Augerson	Network [4]	05/12/2019 -> Email	08/12/19 -> Reply email	10/12/2019 -> Email	17/12/2019 -> Research for the article Augerson 2001	18/12/2019 -> Reply email	18/02/2020 -> Email - Information request	19/02/2020 -> Reply email			
	C2RMF	Marc-André Paulin		17/09/2019 -> Email	18/09/2019 -> Reply email	28/09/2019 -> Phone call	11/10/2019 -> First meeting	18/10/2019 -> Phone call - Reminder	29/10/2019 -> Phone call -	04/12/2019 -> Email - Reminder	12/12/2019 -> Reply email	16/12/2019 -> Phone call - No samples of oil/colophony varnishes found at the C2RMF and at the restoration	17/12/2019 -> Email

												workshop in Versailles		
<i>request</i>	<i>Name</i>	<i>Contact</i>	<i>State</i>	<i>Step 1</i>	<i>Step 2</i>	<i>Step 3</i>	<i>Step 4</i>	<i>Step 5</i>	<i>Step 6</i>	<i>Step 7</i>	<i>Step 8</i>	<i>Step 9</i>	<i>Step 10</i>	
Early oil-based varnishes for ¹⁴C dating	C2RMF	Anne-Solenn Le Hô	Network [4]	25/09/2019 -> Email	27/09/2019 -> Email - Answer - Re-referred to P. Richardin & M.-A. Paulin									
	Musical Instrument Museums Edinburgh	Dr Jonathan Santa Maria Bouquet		04/02/2020 -> CIMCIM 2020 at the Musée de la musique	11/02/2020 -> Email request									
	Ringve Musikkmuseum	Vera de Bruyn-Ouboter		28/01/2020 -> Email	29/01/2020 -> Reply email	31/01/2020 -> Reply email	04/02/2020 -> CIMCIM 2020 at the Musée de la musique	21/02/2020 -> Email - presentation - project report	06/03/2020 -> Reply email - negative reply for the sampling request					
	Violin Society of America	Marilyn Wallin ; Julian Cooke ; Lewis Martinez ; Nicholas Lampo		10/12/2019 -> Email - Information request about varnish sampling and contacts	10/12/2019 -> Email to Nicholas Lampo for VSA contacts	13/12/2019 -> Reply email	19/12/2019 -> Email	08/01/2020 -> Email - Information	20/01/2020 -> Email - Request for a Skype session	20/01/2020 -> Reply answer from Marilyn Wallin	27/01/2020 -> Email - New request for a Skype session	11/02/2020 -> Email - Schedule a short presentation by Skype	20/02/2020 -> Skype session	
	Violon Advisor LLC	Stewart Pollens		10/12/2019 -> Email - Information request on early oil/colophony varnish sampling	12/12/2019 -> Reply email	13/12/2019 -> Email - Request for new contacts among violin dealers	29/12/2019 -> Reply email with new contacts	13/01/2020 -> Email - acknowledgment						
	Atelier Lemaire	Julien Hebras		24-27/10/2019 -> Salon International du Patrimoine, Carrousel du Louvre, Paris	01/11/2019 -> contact LinkedIn	05/11/2019 -> sample prospection attempt								
	Andrew Dipper	Andrew Dipper		10/12/2019 -> Email	10/12/2019 -> Reply email	13/12/2019 -> Reply email with new contacts								

request	Name	Contact	State	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10	
Early oil-based varnishes for ¹⁴ C dating	Bein & Fushi	Alec Fushi	Out [5]	29/12/2019 -> contact via Stewart Pollens	29/01/2020 -> Email									
	Carriage Museum - Château de Versailles	Hélène Delalex		11/05/2020 -> contact via Stéphane Vaiedelich										
	Centre des monuments nationaux	Magali Droguet		12/12/2019 -> Email	17/12/2019 -> Email - information request about varnish sampling for radiocarbon dating									
	Christophe Landon Rare Violons	Christophe Landon		29/12/2019 -> contact via Stewart Pollens	29/01/2020 -> Email									
	Furniture department - Château de Versailles	Elisabeth Caude		12/12/2019 -> Email contact via Marc-André Paulin	17/12/2019 -> Email - information request about varnish sampling for radiocarbon dating	20/12/2019 -> Reply email	07/01/2020 -> Email - Reminder - Scheduled Phone Call	09/01/2020 -> Phone Call - Advised to ask restorers of lacquer such as Anne Jacquin	10/01/2020 -> Email	10/01/2020 -> Reply email				
	Hyogu - Atelier de conservation et restauration d'Art pictural asiatique	Anne Jacquin		09/01/2020 -> contact via Elisabeth Caude	09/01/2020 -> Phone call	09/01/2020 -> Phone call								
	J & A Beares	J & A Beares		29/12/2019 -> contact via Stewart Pollens	29/01/2020 -> Email									
	Kenneth Wareen & Son	James Warren		29/12/2019 -> contact via Stewart Pollens	29/01/2020 -> Email									

	Musée des Arts Décoratifs	Benoît Jenn		12/12/2019 -> contact via Marc-André Paulin									
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<i>request</i>	<i>Name</i>	<i>Contact</i>	<i>State</i>	<i>Step 1</i>	<i>Step 2</i>	<i>Step 3</i>	<i>Step 4</i>	<i>Step 5</i>	<i>Step 6</i>	<i>Step 7</i>	<i>Step 8</i>	<i>Step 9</i>	<i>Step 10</i>	
Early oil-based varnishes for ¹⁴C dating	Musée du Palais Lascaris		Out [5]	16/01/2020 -> contact Likedin via Léa Wegwitz	29/01/2020 -> indirect contact with the curator – negative reply									
	Potter Violin Company			No answer										
	Rare Violins of New York	Bruno Price		29/01/2020 -> Email	30/01/2020 -> Reply email									

Early natural resins for ¹⁴C dating	Denis Caban	Denis Caban	Ex-partnership [2]	07/07/2019 -> discussion on GC-MS applied to colophony with Jérémy Jacob	29/10/2019 -> Email from Jérémy Jacob with information, pictures and samples of old colophony collected at Denis Cabon's workshop								
	MNHN	Bernard Bodo	Potentially qualified [3]	12/02/2020 -> contact via Anne Michelin	24/02/2020 -> reply email	25/02/2020 -> phone call	27/02/2020 -> schedule meeting at the MNKN	10/03/2020 -> study of the samples at the MNHN					
	Antwerpen Universiteit	Vincent Cattersel	Network [4]	13/03/2019 -> LinkedIn contact	07/10/2019 -> new contacts suggested	13/05/2019 -> meeting at the Antwerpen Universiteit							



Linseed oil and colophony from the 1960s and 1970s	Ebay - Tiqin-Songxiang-Violin-Rosin Circa-1960s		Ex-partnership [2]	13/09/2019 -> Search for colophony dated from the 1960s or 1970s among vintage products from Ebay.	04/10/2019 -> Search for Millant-Leroux colophony from the 1960s.	09/10/2019 -> Research for old colophony bags	07/10/2019 -> Order of a Tiqin-Songxiang violin colophony from china dated circa 1960	07/01/2020 -> Chinese colophony from 1960s as confirmed by 14C dating						
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request	Name	Contact	State	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10	
Linseed oil and colophony from the 1960s and 1970s	Ebay - Vintage 1960's CANADA Boiled Linseed Oil TORONTO ELEVATORS - advertising n° 324023305338	eBay - conan7ffx	Ex-partnership [2]	02/02/2020 -> Identification of linseed oil from the 1960s on sale on Ebay	11/03/2020 -> Email									
	KIK-IRPA	Louise Decq		Partnership [1]	07/10/2019 -> Contact via Vincent Cattersel	08/10/2019 -> email request to Louise Decq	18/10/2019 -> reply email with a list of samples	29/11/2019 -> meeting for sampling at KIK-IRPA						

Linseed oil and colophony from the 1960s and 1970s	Sennelier	M. Sennelier	Network [4]	20/03/2019 -> Buying of cold crushed linseed oil "old Holland" Sennelier	28/09/2019 -> Phone call	29/10/2019 -> Phone call – suggestion of new contacts								
	Thierry Moutard-Martin	Thierry Moutard-Martin		10/2020 -> LinkedIn - Post - Call for contributions to find linseed oil and colophony dated from 1960s or 1970s	11/2020 -> suggestion of samples via LinkedIn									

Linseed oil and colophony from the	Royal Talens		Out [5]	13/09/2019 -> Email										
	Kremer Pigmente GmbH & Co. KG	Eva Eis		13/09/2019 -> Email	16/09/2019 -> Negative reply									

1960s and 1970s	Kush Paint Co.		7/10/2019 -> Email										
	Lawter		7/10/2019 -> Email										

request	Name	Contact	State	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10
Varnishes sampling protocol	LacCA project (Lacquered Copper Alloys) - Haute-Ecole Arc Neuchâtel, Switzerland	Julie Schröter	Network [4]	02/09/2019 -> Researchgate	20/10/2019 -> Email - News about the micro-chisels acquisition and question about the sampling practices	22/10/2019 -> Reply email							
	The J. Paul Getty Museum	Arlen Heginbotham		31/10/2019 -> General request for a sampling protocol of varnishes among conservators	14/11/2019 -> Reply email - Stéphanie Auffret (Getty Institute) with the reference of the micro chisel	17/11/2019 -> Reply email							

Early gut strings for ¹⁴ C dating	Atelier Cels	Balthazar Soulier	Partnership [1]	Partnership	18/01/2019-> Email	08/08/2019 -> gut samples	15/09/2020 -> phone call	13/12/2020 -> redirected phone call	14/12/2020 -> phone call to discuss the ¹⁴ C dating results on the gut strings of the Battista violin				
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2. Material corpus for ¹⁴C dating

Table 47. Samples for ¹⁴C measurements

n°sample	Lab code	Sample	Provenance	Sampling date
MGD17	GifA19190.1 GifA19190.2 GifA19190.3 GifA19190.4	gut string	Atelier Cels - Baltazar	16/04/2019
MGD18	GifA19191	gut string	Musée de la musique - Bernardel	16/04/2019
MGD19	GifA19192	gut string	Musée de la musique - Brunner	16/04/2019
MGD20	GifA19193	gut string	Musée de la musique - Tielke	16/04/2019
MGD21	GifA19366	colophony	Laverdure - Landes	01/09/2019
MGD22	GifA19367	colophony	Chine - ebay	29/10/2019
MGD23	GifA19368	colophony	Atelier de lutherie Orléans ⁶¹	29/10/2019
MGD24	GifA19369			
MGD25	GifA19370			
MGD26	GifA19371			
MGD27	GifA19372			
MGD28	GifA19373			
MGD29	GifA19374			
MGD30	GifA19375	linseed oil	Huilerie des Ormes Creux (clarifiée) ⁶²	01/04/2013
MGD31	GifA19376	linseed oil	Sennelier Paris	20/03/2019
MGD32	GifA19142	gut string	Musée de la musique	01/08/2019
MGD33		colophony	Laboratoire KIK-IRPA Bruxelles (USA)	30/11/2019
MGD34	GifA19377	linseed oil	Laboratoire KIK-IRPA Bruxelles	30/11/2019
MGD35		linseed oil	Laboratoire KIK-IRPA Bruxelles	30/11/2019
MGD36		colophony / copal	Laboratoire KIK-IRPA Bruxelles (Portugal)	30/11/2019
MGD37		linseed oil	Huilerie des Ormes Creux (non clarifiée) ²	01/04/2013
MGD38	GifA20175	linseed oil	Vintage 1960's tin Canada full boiled linseed oil Toronto elevators (Canada)	11/03/2020
MGD45	GifA20471	varnish	varnish MGD38 + MGD25 (gros volume)	16/07/2020
MGD46		varnish	varnish MGD31 + MGD22 (petit volume)	16/07/2020
MGD47	GifA20472	varnish	varnish MGD31 + MGD21 (gros volume)	16/07/2020
MGD96		colophony	mon-droguiste.com	19/06/2020
MGD97		linseed oil	Cauvin	19/06/2020
MGD98	GifA20231	historical lacquer	black lacquer qin D.04224 (Q5-2) - CNAM - Musée de la musique	14/01/2019
MGD99	GifA20230	historical wood	wooden support lacquer qin D.04224 (Q5-1) - CNAM - Musée de la musique	14/01/2019
MGD100	GifA20232	historical varnish	Head of Cello "Lafille" sculpture 18 th c. Sampling n°1 - Atelier Nicolas Perrin Boulogne Billancourt	24/06/2020
MGD101	GifA20233	historical varnish	Head of Cello "Lafille" sculpture 18 th c. Sampling n°2 - Atelier Nicolas Perrin Boulogne Billancourt	24/06/2020
MGD102	GifA20234	historical varnish	Cello Jean-Theodore Namy 1773 - Atelier Nicolas Perrin Boulogne Billancourt	24/06/2020

⁶¹ Atelier Denis Caban, Orléans, contact via Jérémy Jacob, LSCE

⁶² Sophie Tirat, PhD samples, 2015, storage at the CRCC, USR3224, Paris

MGD103		colophony	Entreprise Roze, supplied by Costa & Irmãos	01/07/2020
MGD104		turpentine	Laboratoire du Musée de la musique	24/06/2020
MGD123	GifA20339	historical varnish	Louvre - cabinet OA 5468 André-Charles Boulle circa 1700	28/07/2020
MGD124	GifA20340.1 GifA20340.2	historical varnish	Louvre - chest of drawers OA 11193 Bernard II van Risen Burgh - Thomas-Joachim Hébert 1737	28/07/2020
MGD125	GifA20341.1 GifA20341.2 GifA20341.3	historical varnish	Louvre - chest of drawers OA 11193 Bernard II van Risen Burgh - Thomas-Joachim Hébert 1737	28/07/2020
MGD126	GifA20342.1	historical varnish	Compiègne - CMV64-1 - Dragon- left pad - red chips layer - without the preparation layer and the substrate	07/08/2020
MGD126	GifA20342.2	historical varnish	Compiègne - CMV64-1 - Dragon- left pad - from red, gold and green layers to the surface - without the preparation layer and the substrate	07/08/2020
MGD127	GifA20343	historical varnish	Compiègne - CMV64-2 - Dragon- from the red layer to the substrate with the preparation layer	07/08/2020
MGD128	GifA20344	historical varnish	Compiègne - CMV64-3 - Dragon- Layers of oil and pigment, and metallic leaf: preparation layer	07/08/2020
MGD129	GifA20345	historical varnish	Compiègne - CMV64-4 - Dragon- lacquer, silver leaf, then darken upper layer (without preparation and wood)	07/08/2020
MGD130	Gif20346	historical varnish	Compiègne - CMV57006-1 - Eagle	07/08/2020
MGD131	GifA20347	historical varnish	Compiègne - CMV57006-2 - Eagle	07/08/2020
MGD132	GifA20348	historical varnish	Compiègne - CMV57006-3 - Eagle	07/08/2020
MGD133	GifA20349	historical varnish	Compiègne - CMV57006-4 - Eagle	07/08/2020
MGD134	GifA20350	historical varnish	Compiègne - CMV66-1 - Snake	07/08/2020
MGD135	GifA20351	historical varnish	Compiègne - CMV66-2 - Snake	07/08/2020
MGD136	GifA20352	historical varnish	Compiègne - CMV66-3 - Snake	07/08/2020
MGD137	GifA20353	historical varnish	Compiègne - CMV64002-1 – Gold carriage	07/08/2020
MGD138	GifA20354	historical varnish	Compiègne - CMV64002-2 - Gold carriage	07/08/2020
MGD139	GifA20355	hair from a large brush	Compiègne - CMV78-1 - Sedan chair	07/08/2020
MGD140	GifA20356	linseed oil	Compiègne - CMV78-2 - Sedan chair	07/08/2020
MGD141		colophony	L'AS - produits landais-colophane extra	20/08/2020
MGD142	GifA20357	historical varnish	MRAH Brussels - shell and leaf sled - TR88- brown decorative layer	26/08/2020
MGD143	GifA20358	historical varnish	MRAH Brussels - shell and leaf sled - TR88- chips of blue and brown layers	26/08/2020
MGD144	GifA20359	historical varnish	MRAH Brussels - shell and leaf sled - TR88- lead white and Prussian blue preparation layer	26/08/2020
MGD145	GifA20360	historical varnish	MRAH Brussels - Aventurine sled - TR41- Aventurine and preparation layers (vermilion, copper, Prussian blue, oil, colophony)	26/08/2020
MGD146	GifA20361	historical varnish	MRAH Brussels - Red and gold sled - TR1868- chips of vermilion layer, lead white preparation, Prussian blue layer	27/08/2020
MGD147	GifA20362	historical varnish	MRAH Brussels – A red and gold sled - TR1868- preparation layers with lead white and Prussian blue	27/08/2020
MGD148	GifA20363	historical lacquer	red lacquer qin D4224 (Q5-3) CNAM - Musée de la musique	22/09/2020
MGD149	GifA21274	historical varnish	Violin, unknown, 18 ^e S. Mirecourt, E.1993.1.1	14/04/2021
MGD150	GifA21341	historical varnish	Violin, unknown, 18 ^e S. Mirecourt, E.1993.1.1	21/04/2021
MGD151	GifA21342	historical varnish	Violin, Vaillant 18 ^e S. Mirecourt, E.2015.8.1	04/05/2021

Appendix 4. ATR-FTIR spectra

1. Pierre-Saint-Paul violin, c.1740, private collection

The following IRTF-ATR spectra were registered during the preliminary tests to separate wood, glue and successive varnish layers with chisels commonly used by restorers at the Laboratoire du Musée de la musique. However, these tools were unable to provide satisfactory separations for ^{14}C dating application due to the thinness and the complexity of the varnish surface (Figure 135, Figure 136 and Figure 137).

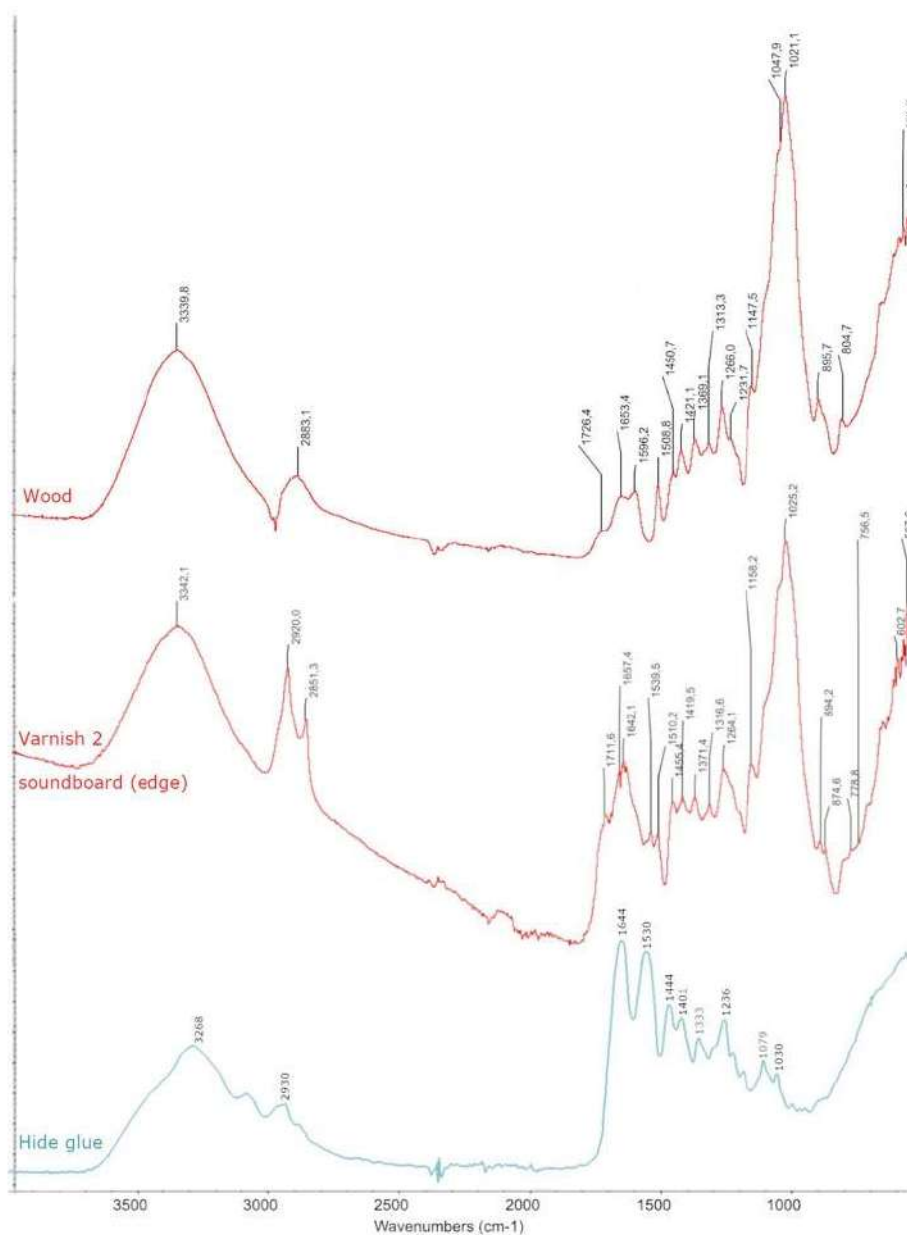


Figure 135. From top to bottom: ATR-FTIR spectrum of wood from the rear side of the soundboard; ATR-FTIR spectrum of varnish (2*); reference spectra of hide glue (database IRUG <http://irug.org/search-spectral-database>)

The upper varnish (2), which was interpreted as a shellac-based varnish applied on the lower varnish 1, provided three samples named as follows: varnish (2) (on the soundboard), varnish (2*) (on an edge of the soundboard) and varnish (2**) (on varnish that had run through a violin soundhole)(Chapter 3 – § 3.1).

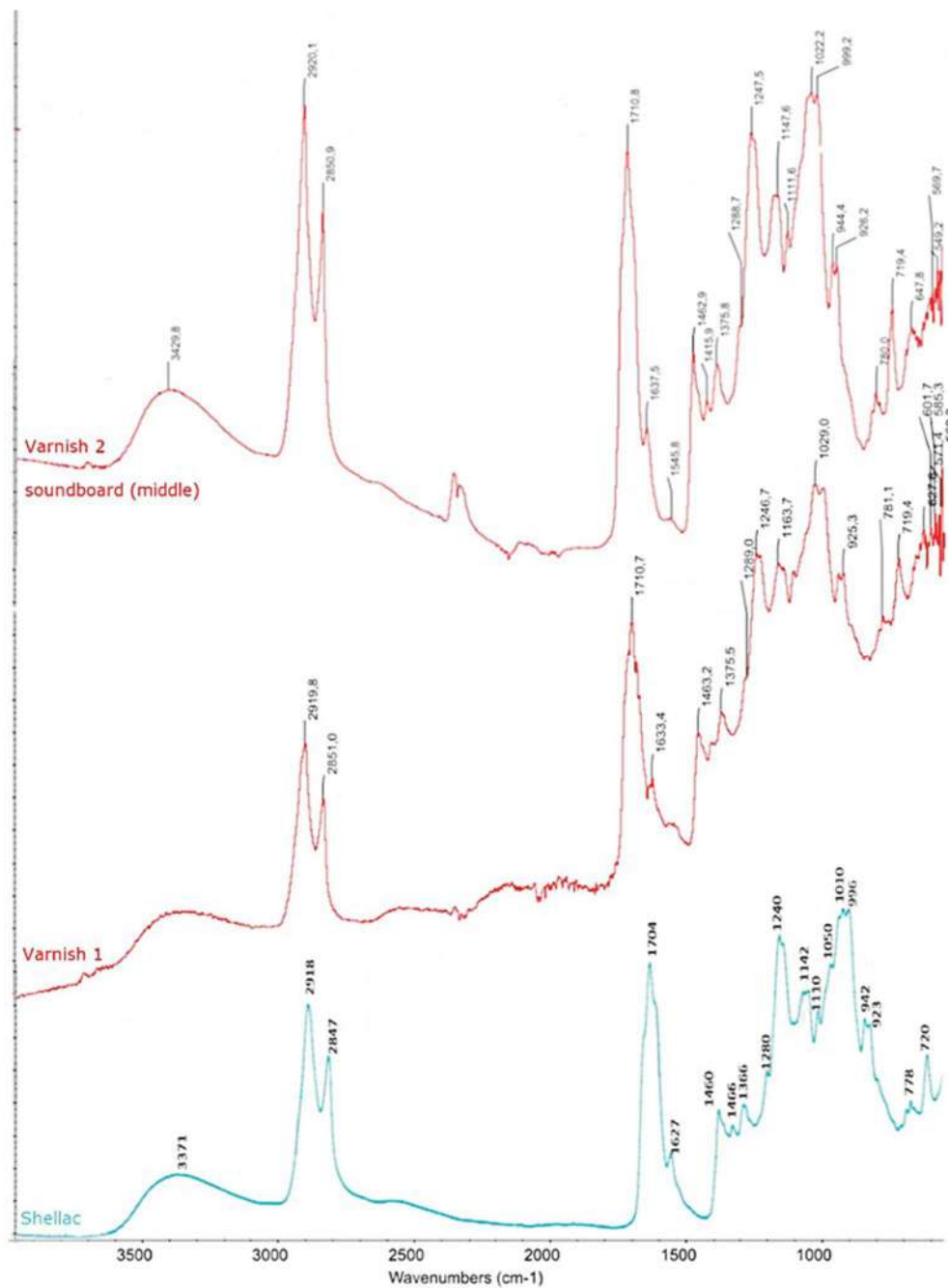


Figure 136. From top to the bottom: ATR-FTIR spectrum of: varnish (2); varnish (1); reference spectra of shellac (database IRUG <http://irug.org/search-spectral-database>)

Figure 135 does not show a real contribution of the amide I, II and III peaks at 1650, 1550, 1452 cm^{-1} from the glue comprising proteinaceous molecules on the spectra collected on the varnish (2*) (Bonizzoni et al., 2014). The varnish sample (2*) might be very thin. Thus, using ATR-FTIR, it is mainly the wood support that is visible. Typical absorption bands of the spectra collected on varnish (1), varnish (2) and varnish (2**) are attributable to resinous diterpenoid and/or

triterpenoid compounds: OH stretching at 3368 cm^{-1} ; C-H aliphatic stretching at 2932 , 2837 cm^{-1} ; C = O broad stretching band absorption at 1709 cm^{-1} ; C = C double bonds of the vinyl group at 1641 cm^{-1} ; C-H absorption at 1451 , 1383 , 889 cm^{-1} ; band characteristic of C-O absorptions at 1249 , 1174 cm^{-1} , C-C stretching band at 1034 cm^{-1} (Bonizzoni et al., 2014).

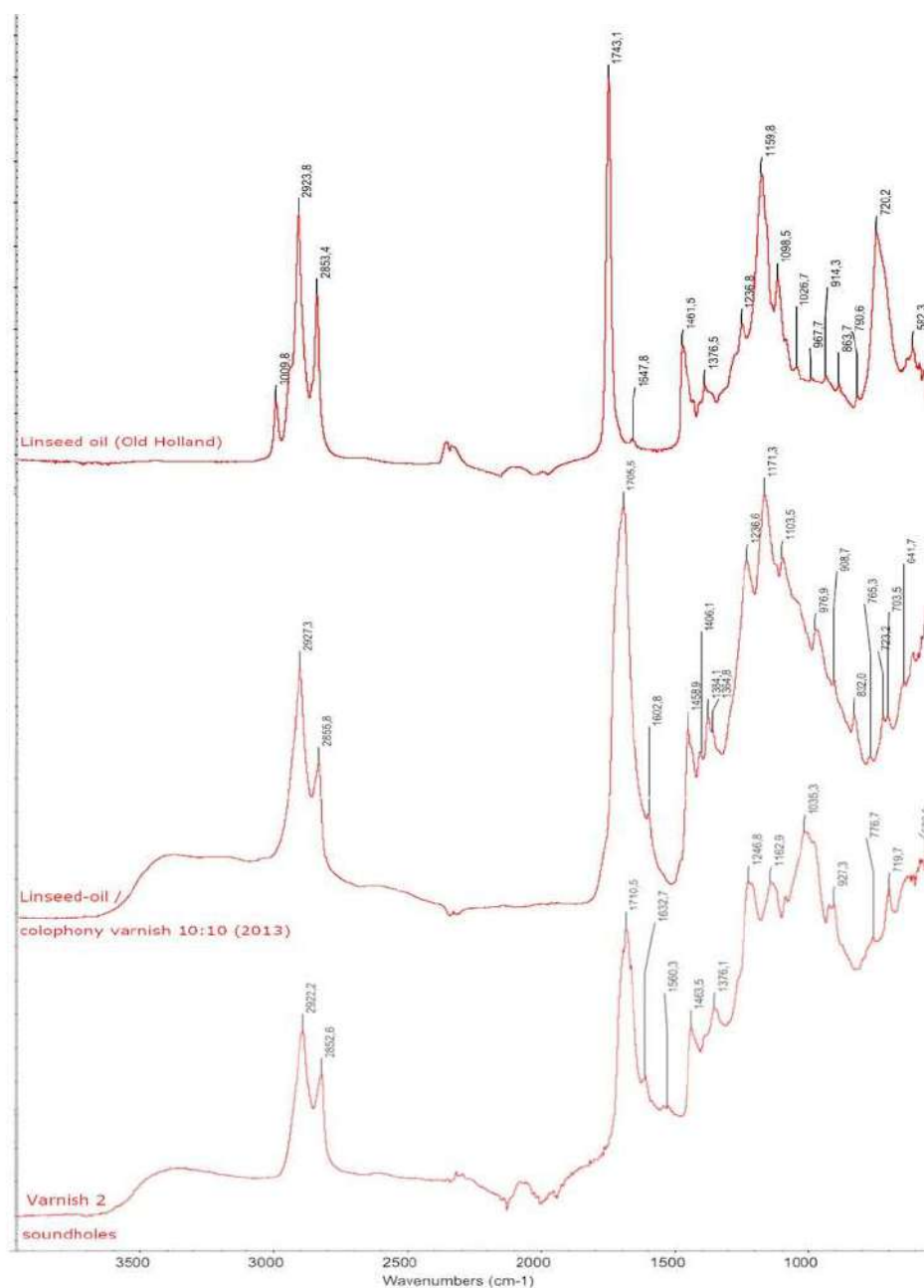


Figure 137. From top to bottom: ATR-FTIR spectrum of: linseed oil (*Old Holland); linseed oil-colophony varnish 10:10 prepared in 2013 (Tirat, 2015); varnish (2**) runs through a violin soundhole

This subject was not treated during this PhD. However, we note that the possibility of discriminating the different organic binders used in violin varnishes was studied in previous research by combining Raman spectrometry and ATR-IRTF (Daher et al., 2010, 2013, 2014a, 2014b).

2. Non-inventoried head of a broken bow, Musée de la musique collection

This non-inventoried head of a broken bow (named E0) comprises two broken pieces glued together according to visual examination. A botanical pre-analysis based on transverse and tangential microscopic images suggests that the lower broken part is more likely made of yew wood⁶³. The entry of the object into the Musée de la musique collection is not well documented.

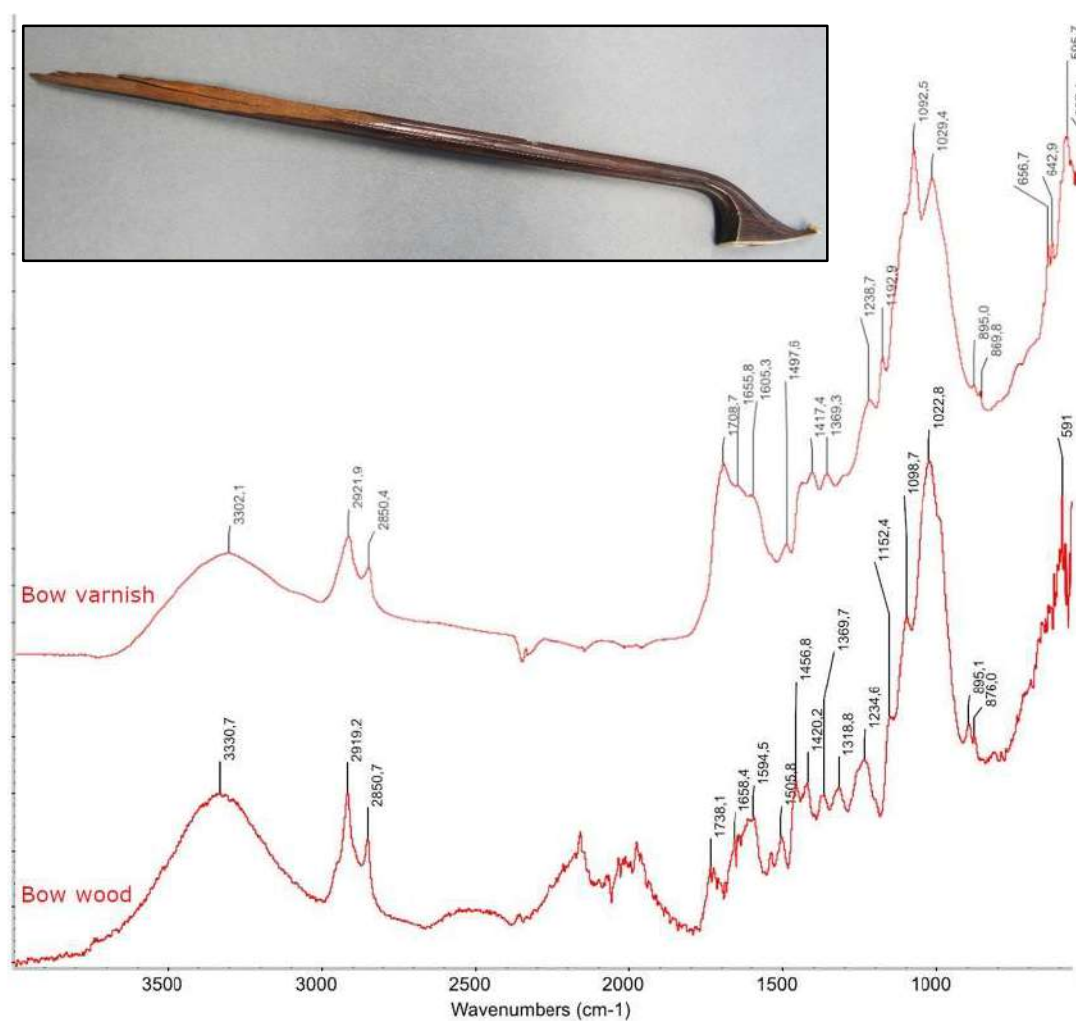


Figure 138. From top to bottom: Picture of the bow E0; ATR-FTIR spectrum of the varnish sample taken with a common chisel; ATR-FTIR spectrum of the wood sample taken with a common chisel

A sampling test of the varnish was performed on the bow E0 with chisels commonly used by restorers at the Laboratoire du Musée de la musique. However, the IRTF-ATR spectra yielded

⁶³ Micrographs taken by Anne Houssay with a Zeiss Axio Scope.A1 Vario optical microscope at the Laboratoire du Musée de la Musique and personal communication by Anne Houssay, 2018/12/06

show common peaks between the wood and varnish layers, showing again the difficulty of properly separating the varnish layer for ^{14}C dating using ordinary tools (Figure 138).

Although the spectra are difficult to dissociate, a peak at 1708 cm^{-1} was observed for the varnish and it can be assumed that it comprises diterpenic and/or triterpenoid aged resins (Bonizzoni et al., 2014).

3. References

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- Daher C., Drieu L., Bellot-Gurlet L., Percot A., Paris C. and Le Hô A.-S. (2014a) Combined approach of FT-Raman, SERS and IR micro-ATR spectroscopies to enlighten ancient technologies of painted and varnished works of art: Study of the technology of french decorative arts objects. *Journal of Raman Spectroscopy* **45**, 1207–1214.
- Daher C., Paris C., Le Hô A.-S., Bellot-Gurlet L. and Échard J.-P. (2010) A joint use of Raman and infrared spectroscopies for the identification of natural organic media used in ancient varnishes. *Journal of Raman Spectroscopy* **41**, 1494–1499.
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Appendix 5. Gut strings

Pictures were taken under visible light (Figure 139) and using an optical microscope (Figure 140, Figure 141) of:

- i- a gut string (G note) from a Bernardel cello, n°506, 1896, Paris, and dated using ¹⁴C dating.
- ii- a gut string (G note) of a violin that belonged to Paul Baillot, a violin teacher at the Conservatoire de Paris between 1848 and 1878 and probably teaching until 1886.

There are strong visual similarities between the two wound gut strings:

- o the same color of the gut,
- o the same aspect of copper wires (the wire used for the cello is of course larger than the one used for the violin)
- o the same speed of rotation of the wire. When the distance between two successive turns of the copper wire wound round the gut string increases at the end of the string, the copper wires have the same angles with the gut strings,
- o the same winding pitch of the gut strips.

Therefore, there are several material arguments indicating that the studied string from the Bernardel cello, n°506, 1896, Paris is typical of the period 1870-1900 in Paris.

A perspective could be to compare the winding pitch of 19th c. gut strings with pre-industrial gut strings with a twisted structure (previously cut into strips or not).

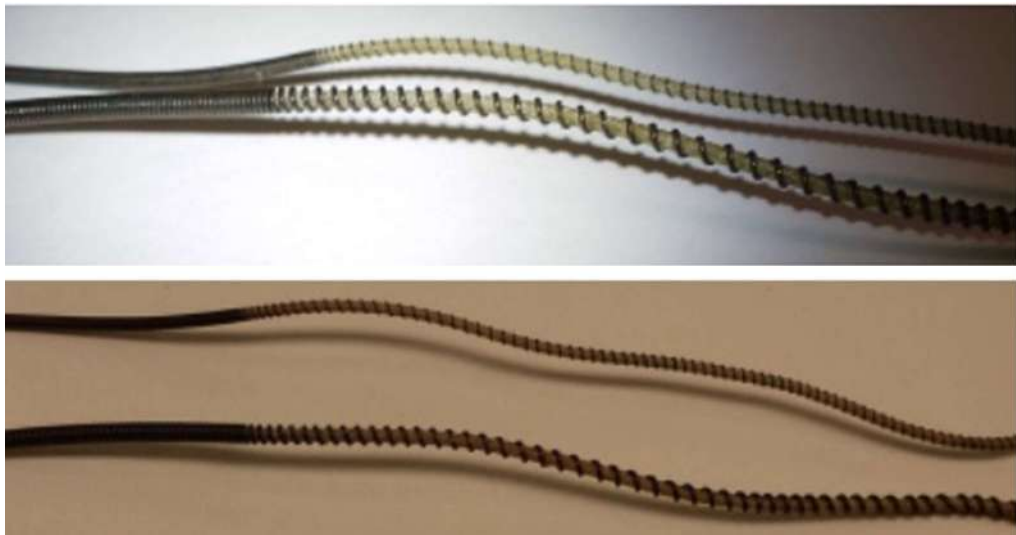


Figure 139. Comparison of the gut strings, Bernardel 1896 (left) and Baillot c.1850 (right)

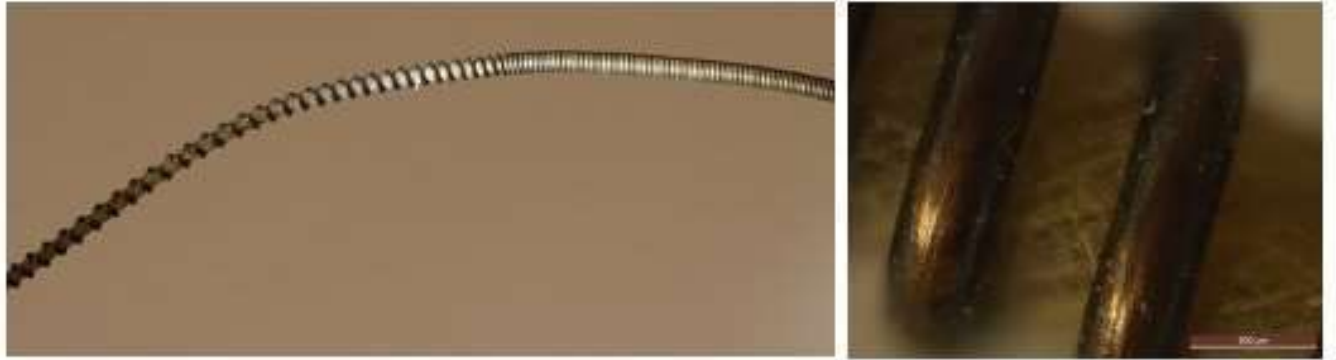


Figure 140. A gut string from a Bernardel cello, n°506, 1896, Paris.



Figure 141. A gut string (G note) from P. Baillot, c.185

Appendix 6. Sr geochemistry investigations

1. Soil/resin/colophony prospection

1.1. Participatory science call

Here is the participatory science call that was launched to collect pine soil-resin couples from defined localizations and from the tree species commonly used for colophony production. The call was broadcast on the website of the Philharmonie de Paris in French and English from April to July 2020 during the Covid-19 pandemic:

<https://philharmoniedeparis.fr/fr/magazine/breves/pins-et-confinement>

<https://philharmoniedeparis.fr/fr/magazine/breves/pines-and-quarantine>



PINE AND QUARANTINE

If you live in a region where pine trees grow, the Laboratoire du Musée de la musique in Paris has an important mission for you.

While we are stuck at home, the resin is rising in the pine tree trunks. Pine resin is used to produce colophony, which is then used to make oil-based varnishes, particularly for violins.

Pine resin contains many different molecules and atoms and one of them is strontium, which can appear in different variations called isotopes.

Why should you care about strontium isotopes? The same ratio of strontium isotopes that are found in the pine resin can also be found in the soil in which the tree grew.

Can you see where this is going? That's right! The strontium isotopes we can detect in the pine resin can be found in the varnish on violins, creating a GPS tracking system for old violins. Pretty cool, huh?

By time the lock-down is over, the season for harvesting the resin will also be over. So if you or your friends have pine trees nearby, don't hesitate to collect some samples.

As a knowledgeable research technician, please collect the following:

- pine resin
- soil sample at the base of the pine

PINE RESIN AND SOIL SAMPLES

① Find a conifer and identify it:

Pine species will do (Aleppo pine, Scots pines, Maritime pines, Stone pines ...)

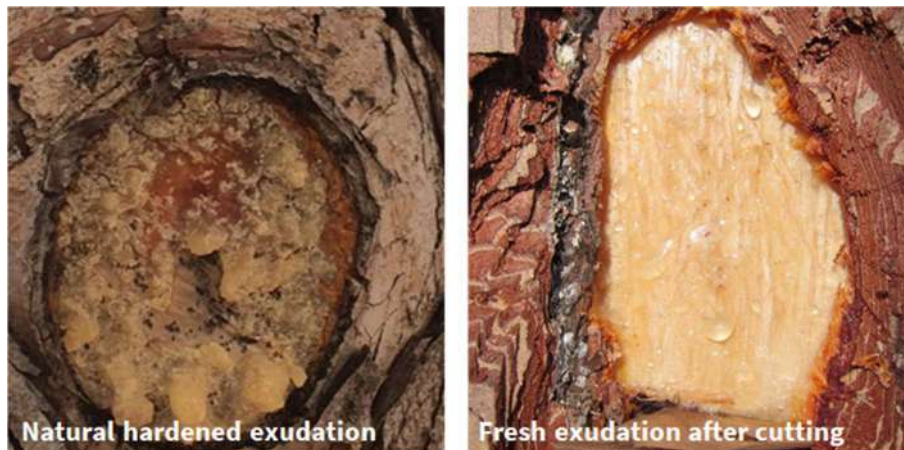
Silver firs (*Abies alba*)

Larches

If any doubt, use <https://plantnet.org/en/> or send us a piece of a branch, or wood, or a pine cone.

② Take a resin sample already exuded by the tree or slightly cut the bark to reach the sapwood with a pocket knife (caution: be gentle with the tree)

Tip: You can also staple a bag at the base of the cut and go do something else while waiting for the resin to flow out.



③ Take a soil sample at the base of the tree

One tablespoon is enough. Put the resin and soil in separate freezer bags.

Note the geographical coordinates on the bag using a compass application.

Take some nice pictures of the tree and your work.



If you have any questions, contact us by email at the address below and send us your pictures and the geographical coordinates of your tree to the same address:

mgdurier@cite-musique.fr

And finally, send us these samples by post to the following address before June 1st:

M.G Durier - Pine and quarantine

XXXXXX – FRANCE

1.2. Contact with professionals

Professionals were also contacted and asked to contribute to the collection of pine soil-resin-colophony trios from defined localizations and from the tree species commonly used for colophony production (Table 48). Sampling was delayed due to the Covid-19 pandemic.

Table 48. Recapitulative table of samples prospection

request	Name	Contact	State	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10
Pine resins from well-identified provenance (soil/resin/colophony)	Costa & Irmaos	Ana Rita Gomes	Partnership	24/01/2020 -> contact email with Irmaos following a recommendation by Roze company	31/01/2020 -> email reply by the Quality Department of Irmaos	11/02//20 -> research of relevant sampling opportunities by Irmaos	02/03/20 -> research for colophony with a specific origin by Irmaos	20/03/20 -> sampling expected for June/July 2020	21/07/20 -> email sampling delays due to the pandemic	8/04/21 -> email to contact again after the pandemic	19/05/21 -> email asking for further information about the sampling	24/06/21 -> Sampling of soil, pine and colophony in a specific area by Irmaos	08/07/21 -> Samples sent by Irmaos to the LSCE
Pine resins from well-identified provenance (soil/resin/colophony)	Galipot	Samuel Aubert	Partnership	29/04/2020 -> contact email following a recommendation by Biolandes	01/05/2020 -> Phone Call	01/05/2020 -> Email	27/05/2020 -> Email - Reminder for sampling	27/05/2020 -> Email - Phone call scheduled	23/06/2020 -> Samples sent by Samuel Auber to the LSCE				
Pine resins from well-identified provenance	D&P Green	Olivier Ségouin / Sandrine Charrière	Partnership	11/03/2019 -> Contact via the website https://www.domaines-et-patrimoine.fr/	15/04/2019 -> Email	05/2019 -> Receipt of the order for 100g of colophony from the South-West of France (Landes)	09/01/2020 -> Contacts information	09/01/2020 -> Email - Information request	13/01/2020 -> Phone Call	24/02/2020 -> Email - Request			
Pine resins from well-identified provenance	Biolandes	Emilie Angles	Network	17/02/2020 -> LinkedIn message	18/02/2020 -> LinkedIn message	20/02/2020 -> LinkedIn message	20/02/2020 -> Email - Information request	24/02/2020 -> Email - Reminder	24/02/2020 -> Email - Answer from Emilie Angles - request for further information about pine species	26/02/2020 -> Email	15/04/2020 -> Reply email – from Biolandes	19/04/2020 -> Email – email contact of M. Luc Leneveu from Biogemme and Samuel Aubert from Galipot	

2. Corpus soil/resin couples

Table 49. Corpus soil/resin couples and soil/resin/colophony trios

n°sample	Sample	Provenance	Date	Geographical origin	Site
MGD39E	pine trunk	<i>Pinus halepensis</i> - Campagne Pastrée - Marseille	09/03/2020	Campagne Pastrée. 13008 Marseille (43°15'08" N - 5°22'21" E 50m above sea level)	6
MGD39R	pine resin	<i>Pinus halepensis</i> - Campagne Pastrée - Marseille	09/03/2020	Campagne Pastrée. 13008 Marseille (43°15'08" N - 5°22'21" E, 50m above sea level)	6
MGD40	soil	<i>Pinus halepensis</i> - Campagne Pastrée - Marseille	09/03/2020	Campagne Pastrée, 13008 Marseille (43°15'08" N - 5°22'21" E, 50m above sea level)	6
MGD41	pine resin	<i>Pinus sylvestris</i> - Fontainebleau	15/03/2020	Fontainebleau (48°20'43" N / 2°41'11" E)	7
MGD42	soil	<i>Pinus sylvestris</i> - Fontainebleau	15/03/2020	Fontainebleau (48°20'43" N / 2°41'11" E)	7
MGD43	pine resin	<i>Pinus pinea</i> - Malmousque - Marseille	29/03/2020	Malmousque, 13008 Marseille (43°16'50" N / 5°20'52" E, 10m above sea level)	8
MGD44	soil	<i>Pinus pinea</i> - Malmousque - Marseille	29/03/2020	Malmousque, 13008 Marseille (43°16'50" N / 5°20'52" E, 10m above sea level)	8
MGD48	pine resin	<i>Pinus sylvestris</i> - Puy-en-Velay	20/05/2020	Arraules, Haute-Loire (04°08'41.6" E / 45°03'54.2" N, 1022m above sea level)	9
MGD49	soil	<i>Pinus sylvestris</i> - Puy-en-Velay	20/05/2020	Arraules, Haute-Loire (04°08'41.6" E / 45°03'54.2" N, 1022m above sea level)	9
MGD50	pine resin	<i>Pinus sylvestris</i> - Clermond-Ferrand	01/04/2020	Saint-Quintin-sur-Sioule 63440 (46°06'02" N / 3°11'57" E)	10
MGD51	soil	<i>Pinus sylvestris</i> - Clermond-Ferrand	01/04/2020	Saint-Quintin-sur-Sioule 63440 (46°06'02" N / 3°11'57" E)	10
MGD52	pine resin	<i>Pinus halepensis</i> - Toulon	21/04/2020	Sanary-sur-mer 83110 (43°7'26" N / 5°48'25" E)	11
MGD53	soil	<i>Pinus halepensis</i> - Toulon	21/04/2020	Sanary-sur-mer 83110 (43°7'26" N / 5°48'25" E)	11

MGD54	pine resin	<i>Pinus sylvestris</i> - Saint-Etienne - Loire	15/04/2020	Saint-Etienne 42100 (45°24'43" N / 04°26'06" E)	12
MGD55	soil	<i>Pinus sylvestris</i> - Saint-Etienne - Loire	15/04/2020	Saint-Etienne 42100 (45°24'43" N / 04°26'06" E)	12
MGD56	pine resin	<i>Pinus pinaster</i> - Drôme	23/04/2020	Saillans 26340 (44°41'49" N / 5°9'35" E)	13
MGD57	soil	<i>Pinus pinaster</i> - Drôme	23/04/2020	Saillans 26340 (44°41'49" N / 5°9'35" E)	13
MGD58	pine resin	<i>Pinus nigra</i> - Drôme	07/05/2020	La Laupie 26740 Drôme (44°36'4" N / 4°50'45" E)	14
MGD59	soil	<i>Pinus nigra</i> - Drôme	07/05/2020	La Laupie 26740 Drôme (44°36'4" N / 4°50'45" E)	14
MGD60	pine resin	pin de Bandol - Provence-Alpes	19/05/2020	Le Beausset, Provence-Alpes-Côte d'Azur (43°10'52" N / 5°48'30" Est)	15
MGD61	soil	pin de Bandol - Provence-Alpes	19/05/2020	Le Beausset, Provence-Alpes-Côte d'Azur (43°10'52" N / 5°48'30" E)	15
MGD62	pine resin	<i>Pinus pinaster</i> - Essonnes	18/05/2020	91150 Étampes (48°25'54" N / 2°10'39" E)	16
MGD63	soil	<i>Pinus pinaster</i> - Essonnes	18/05/2020	91150 Étampes (48°25'54" N / 2°10'39" E)	16
MGD64	pine resin	<i>Pinus halepensis</i> - Côte-Azur- Nice	04/05/2020	Roquefort-les-pins 063330, Nice (43°41'25" N / 7°2'18" E)	17
MGD65	soil	<i>Pinus halepensis</i> - Côte-Azur- Nice	04/05/2020	Roquefort-les-pins 063330, Nice (43°41'25" N / 7°2'18" E)	17
MGD66	pine resin	<i>Pinus sylvestris</i> - Orsay	12/04/2020	Orsay (48°41'55" N / 2°11'36" E)	18
MGD67	soil	<i>Pinus sylvestris</i> - Orsay	12/04/2020	Orsay (48°41'55" N / 2°11'36" E)	18
MGD68	pine resin	<i>Pinus sylvestris</i> - Orsay	12/04/2020	Orsay (48°35'54" N / 2°11'50" E)	18
MGD69	soil	<i>Pinus sylvestris</i> - Orsay	12/04/2020	Orsay (48°35'54" N / 2°11'50" E)	18
MGD70	pine resin	<i>Pinus sylvestris</i> - Orsay	12/04/2020	Orsay (48°35'54" N / 2°11'50" E)	18
MGD71	soil	<i>Pinus sylvestris</i> - Orsay	12/04/2020	Orsay (48°35'54" N / 2°11'50" E)	18
MGD72	pine resin	<i>Pinus sylvestris</i> - Orsay	13/04/2020	Orsay (48°41'50" N / 2°11'42" E)	18
MGD73	soil	<i>Pinus sylvestris</i> - Orsay	13/04/2020	Orsay (48°41'50" N / 2°11'42" E)	18
MGD74	pine resin	<i>Pinus pinaster</i> - Landes	29/05/2020	South of the Landes (43°33'45" N / 1°21'28" O)	19
MGD75	soil	<i>Pinus pinaster</i> - Landes	29/05/2020	South of the Landes (43°33'45" N / 1°21'28" O)	19
MGD76	pine resin	1 - <i>Pinus halepensis</i> - Avignon	26/05/2020	84914 Avignon (43°38'07.8"N / 5°09'44.8"E)	20

MGD77	soil	1 - <i>Pinus halepensis</i> - Avignon	26/05/2020	84914 Avignon (43°38'07.8"N / 5°09'44.8"E)	20
MGD78	pine resin	2 - <i>Pinus halepensis</i> - Avignon	26/05/2020	84914 Avignon (43°38'20.0"N / 5°09'57.4"E)	20
MGD79	soil	2 - <i>Pinus halepensis</i> - Avignon	26/05/2020	84914 Avignon (43°38'20.0"N / 5°09'57.4"E)	20
MGD80	pine resin	3 - <i>Pinus halepensis</i> - Avignon	26/05/2020	84914 Avignon (43°38'16.7"N / 5°09'59.8"E)	20
MGD81	soil	3 - <i>Pinus halepensis</i> - Avignon	26/05/2020	84914 Avignon (43°38'16.7"N / 5°09'59.8"E)	20
MGD82	pine resin	4 - <i>Pinus halepensis</i> - Avignon	26/05/2020	84914 Avignon (43°38'15.7"N / 5°10'01.1"E)	20
MGD83	soil	4 - <i>Pinus halepensis</i> - Avignon	26/05/2020	84914 Avignon (43°38'15.7"N / 5°10'01.1"E)	20
MGD84	pine resin	5 - <i>Pinus halepensis</i> - Avignon	26/05/2020	84914 Avignon (43°38'21.5"N / 5°09'43.4"E)	20
MGD85	soil	5 - <i>Pinus halepensis</i> - Avignon	26/05/2020	84914 Avignon (43°38'21.5"N / 5°09'43.4"E)	20
MGD86	pine resin	6 - <i>Pinus halepensis</i> – Avignon	26/05/2020	84914 Avignon (43°38'21.7"N / 5°07'32.7"E)	20
MGD87	soil	6 - <i>Pinus halepensis</i> – Avignon	26/05/2020	84914 Avignon (43°38'21.7"N / 5°07'32.7"E)	20
MGD88	pine resin	7 - <i>Pinus halepensis</i> – Avignon	26/05/2020	84914 Avignon (43°38'33.8"N / 5°07'38.3"E)	20
MGD89	soil	7 - <i>Pinus halepensis</i> – Avignon	26/05/2020	84914 Avignon (43°38'33.8"N / 5°07'38.3"E)	20
MGD92	pine resin	<i>Pinus halepensis</i>	26/05/2020	13400 Aubagne (43°19'48"N / 5°34'52"E)	22
MGD93	soil	<i>Pinus halepensis</i>	26/05/2020	13400 Aubagne (43°19'48"N / 5°34'52"E)	22
MGD94	pine resin	<i>Pinus sylvestris</i>	11/06/2020	91250 Morsang-sur-seine (48°32'5" N / 2°31'49" E)	23
MGD95	soil	<i>Pinus sylvestris</i>	11/06/2020	91250 Morsang-sur-seine (48°32'5" N / 2°31'49" E)	23
MGD105	pine resin	<i>Pinus halepensis</i> – Drôme	23/06/2020	26170 Propiac (44°16'45"N / 5°14'26"E /Alt. 397,4 m)	28
MGD108	soil	<i>Pinus halepensis</i> – Drôme	23/06/2020	26170 Propiac (44°16'45"N / 5°14'26"E /Alt. 397,4 m)	28
MGD109	pine resin	<i>Pinus pinea</i> - La Motte 84240	01/07/2020	84240 La Motte (43°46'44"N / 005°31'25"E)	29

MGD110	soil	<i>Pinus pinea</i> - La Motte 84240	01/07/2020	84240 La Motte (43°46'44"N / 005°31'25"E)	29
MGD111	pine resin	<i>Pinus sylvestris</i> - La Motte 84240	01/07/2020	84240 La Motte (43° 46'01"N / 5°31'12"E)	29
MGD112	soil	<i>Pinus sylvestris</i> - La Motte 84240	01/07/2020	84240 La Motte (43°46'01"N / 5°31'12"E)	29
MGD113	cedar resin	cedar - La Motte 84240	01/07/2020	84240 La Motte (43°46'51"N / 5°31'24"E)	29
MGD114	soil	cedar - La Motte 84240	01/07/2020	84240 La Motte (43°46'51"N / 5°31'24"E)	29
MGD115	cedar resin	cedar Atlas - La Motte 84240	01/07/2020	84240 La Motte (43°46'51"N / 5°31'22"E)	29
MGD116	soil	cedar Atlas - La Motte 84240	01/07/2020	84240 La Motte (43°46'51"N / 5°31'22"E)	29
MGD117	spruce resin	Picea - 26210 Epinouze	05/07/2020	26210 Epinouze (45°18'33.73"N / 4°55'37.98"E)	30
MGD118	soil	Picea - 26210 Epinouze	05/07/2020	26211 Epinouze (45°18'33.73"N / 4°55'37.98"E)	30
MGD119	pine resin	1 - 26210 Epinouze	05/07/2020	26212 Epinouze (45°18'33.73"N / 4°55'37.98"E)	30
MGD120	soil	1 - 26210 Epinouze	05/07/2020	26213 Epinouze (45°18'33.73"N / 4°55'37.98"E)	30
MGD121	pine resin	3 - 26210 Epinouze	05/07/2020	26214 Epinouze (45°18'33.73"N / 4°55'37.98"E)	30
MGD122	soil	3 - 26210 Epinouze	05/07/2020	26215 Epinouze (5°18'33.73"N / 4°55'37.98"E)	30
MGD152	pine resin	<i>Pinus Pinea</i> - Costa Irmaos, Alcochete, Setubal district, Portugal	14/04/2021	38°45'19.22"N / -8°57'39.10"W	33
MGD153	colophony	<i>Pinus Pinea</i> - Costa Irmaos, Alcochete, Setubal district, Portugal	14/04/2021	38°45'19.22"N / -8°57'39.10"W	33
MGD154	soil	<i>Pinus Pinea</i> - Costa Irmaos, Alcochete, Setubal district, Portugal	14/04/2021	38°45'19.22"N / -8°57'39.10"W	33

3. Sr protocols

3 methods for Sr isotopic measurements on honey (Lorna Foliot)

1 - Chemical digestion using HNO₃ and HClO₄: 1g of honey, then add 15mL HNO₃ 67% (beware of strong degassing). After almost dry evaporation, add 10mL HNO₃ 67% and 5mL of concentrated HClO₄ and finally evaporate at 120°C.

2 - Chemical digestion using HNO₃ and H₂O₂: 1g of honey, then add 10mL HNO₃ 67% and 5mL H₂O₂ (beware of strong degassing) and finally evaporate.

3 - Dry digestion: oven at 450°C during 8h.

4 - The microwave method: 1g of honey and 8mL HNO₃ 67% then 10min to reach the temperature of 180°C and finally 20 min at 180°C.

Samples are then taken up in a 3 M HNO₃ solution and loaded onto cation exchange columns charged with Sr-Spec (Eichrome Inc.) resin to separate the purified strontium fractions.

Protocol Sr isotopy in soil (Caroline Gauthier):

- Combustion in an oven at 800°C during 10h.
- Ammonium acetate 1M during 24h at room temperature (i.e. 2.31mg for 30mL of water):
add 10mL of ammonium acetate 1M to 1g of soil
- Take up the supernatant and evaporate the solution

Protocol Sr isotopy in plants (Caroline Gauthier):

- Combustion in an oven at 555°C during 12h with an oven temperature ramp in a span of 2h:
+ 80°C every 20 min until 550°C
(be careful around 300°C when the combustion temperature of plants is reached)
- HNO₃ 15N -> hot evaporation 2h
- H₂O₂ 30% -> hot evaporation during 1 day

4. Samples and applied protocols

Table 50. Summary of the samples and the tested protocols A to F

Sample ID	Lab ID	Material	weight (mg)	vol. (mL)	Lab conditions
Blank	8221	∅	0		Savillex™, protocol A
MGD21	8222	colophony	29.1		Savillex™, protocol A
MGD21	8223	colophony	51.5		Savillex™, protocol A

MGD21	8224	colophony	102.1		Savillex™, protocol A
MGD21	8226	colophony	30.5		Savillex™, protocol A
MGD104	x	turpentine	-	10 mL	Savillex™, protocol A
MDG105	x	pine resin	8597.5		Savillex™, protocol A
MGD31	x	linseed oil	-	10 mL	Savillex™, protocol A
MGD38	x	linseed oil	-	10 mL	Savillex™, protocol A
MGD21	8296	colophony	201.7		powder in crucible, protocol B
MGD21	8297	colophony	500		powder in crucible, protocol B
MGD21	8298	colophony	1000		powder in crucible, protocol B
Blank	8299	∅	0		crucible, protocol B
MGD21	8415	colophony	500.2		powder in crucible, protocol B
MGD21	8416	colophony	2001.6		powder in crucible, protocol B
Blank	8414	∅	0		lumps in crucible, protocol B
MGD76	-	pine resin	1530.5		crucible, protocol B
MGD39R	-	pine resin	1008.4		crucible, protocol B
MGD39E	-	pine bark	3304.1		crucible, protocol B
MGD90	-	colophony	2009.6		crucible, protocol B
MGD74	-	pine resin	1043.8		crucible, protocol B
MGD91	-	colophony	2020.0		crucible, protocol B
MGD25	-	colophony	1028.1		crucible, protocol B
MGD54	-	pine resin	1053.6		crucible, protocol B
MGD103	-	colophony	5177.4		crucible, protocol B
MGD106	-	colophony	1973		crucible, protocol B
MGD107	-	colophony	1087.7		crucible, protocol B
MGD105	-	pine resin	2155.5		crucible, protocol C
MGD104	-	turpentine	-	5 mL	crucible, protocol C
MGD38	-	linseed oil	-	5 mL	crucible, protocol C
MGD38	-	linseed oil	-	10 mL	crucible, protocol B
MGD31	-	linseed oil	-	5 mL	crucible, protocol C

MGD31	-	linseed oil	-	10 mL	crucible, protocol B
MGD30	-	linseed oil	-	5 mL	crucible, protocol C
MGD30	-	linseed oil	-	10 mL	crucible, protocol B
Blank 1	-	∅	0		crucible, protocol B
Blank 2	-	∅	0		crucible, protocol B
MGD45	-	linseed oil MGD38 + colophony MGD25	849.5 + 350.3		1g of varnish 70:30, crucible, protocol B
MGD47	-	linseed oil MGD31 + colophony MGD21	825.7 + 400.8		1g of varnish 70:30, crucible, protocol B
JCT 2	-	standard 20 ppb JCT	-	5 mL	crucible, protocol B
JCT 2	-	standard 20 ppb JCT	-	5 mL	crucible, protocol B
NBS 1	-	standard 40 ppb NBS	-	5 mL	crucible, protocol B
NBS 2	-	standard 40 ppb NBS	-	5 mL	crucible, protocol B
Blank	9096	∅	0		qualified crucible, take up with 2mL MilliQ
MGD31	9093	linseed oil	-	10 mL	qualified crucible, take up with 2mL MilliQ
MGD31	9097	linseed oil + aluminium	-	10 mL	qualified crucible + aluminium foil, take up with 2mL MilliQ
Blank	9098	∅ + aluminium	0		qualified crucible + aluminium foil, take up with 2mL MilliQ
MGD38	9094	linseed oil	-	10 mL	qualified crucible, take up with 2mL MilliQ
MGD105	9095	pine resin	-	10 mL	qualified crucible, take up with 2mL MilliQ
Blank	9086	∅	0		qualified crucible, take up with 2mL MilliQ
JCT	9085	JCT 1000 ppm	-	0.6 mL	qualified crucible, take up with 2mL MilliQ
NBS	9084	NBS 987	-	1 mL	qualified crucible, take up with 2mL MilliQ
MGD21	9080	colophony	2197.4		qualified crucible, take up with 2mL MilliQ

MGD74	9081	pine resin	1067.0		qualified crucible, take up with 2mL MilliQ
MGD54	9082	pine resin	1277.0		qualified crucible, take up with 2mL MilliQ
MGD90	9083	pine resin	2088.0		qualified crucible, take up with 2mL MilliQ
Blank	9099	∅	0		qualified crucible, take up with 2mL MilliQ
JCT	9091	JCT 1000 ppm	-	0.3 mL	qualified crucible, take up with 2mL MilliQ
MGD103	9088	colophony	2069.7		qualified crucible, take up with 2mL MilliQ
MGD107	9089	colophony	9089		qualified crucible, take up with 2mL MilliQ
MGD39E	9090	pine bark	2245.5		qualified crucible, take up with 2mL MilliQ
NBS	9092	NBS 987	-	0.5 mL	qualified crucible, take up with 2mL MilliQ
MGD25	9087	colophony	2031.0		qualified crucible, take up with 2mL MilliQ
MGD40	-	soil	1110.9		crucible, protocol F
MGD55	-	soil	1072.0		crucible, protocol F
MGD75	-	soil	1174.1		crucible, protocol F
MGD77	-	soil	1086.2		crucible, protocol F
MGD108	-	soil	1143.1		crucible, protocol F

5. Sr isotope measurements

Table 51. Labelled and classified measured samples for Sr isotope measurements

Site ID	Material	Sample ID	Lab ID	weight (g)	vol. (mL)	⁸⁷ Sr/ ⁸⁶ Sr ratio	
21	colophony	MGD90	9083	2088.0		0.7106	replicable
1	colophony	MGD21	8415	500.16		0.7135	replicable
			8416	2001.6		0.7133	replicable

			2020-juin	5072.6		0.7136	replicable
3	colophony	MGD25	9087	2031.0		0.7100	replicable
26	colophony	MGD103	9088	2069.7		0.7164	replicable
32	linseed oil	MGD38	2020-juin	-	5 mL	0.7105	replicable
			9094	-	10 mL	0.7104	replicable
5	linseed oil	MGD31	9093	-	10 mL	0.7117	replicable
			9097	-	10 mL	0.7105	replicable
19	pine resin	MGD74	9081	1067.0		0.7091	replicable
	soil	MGD75	2020-juin	1174.1		0.7095	replicable
6	bark	MGD39E	2020-juin	3304.1		0.7084	replicable
	bark	MGD39E	9090	2245.5		0.7083	replicable
	soil	MGD40	2020-juin	1110.9		0.7081	replicable
12	pine resin	MGD54	9082	1277.0		0.7164	replicable
	soil	MGD55	2020-juin	1072.0		0.7177	replicable
28	soil	MGD108	2020-juin	1143.1		0.7076	replicable
	colophony	MGD107	9089	2128.7		0.7091	replicable
		MGD106	2020-juin	1973.0		0.7128	invalid
	pine resin	MGD105	9095	8597.5		0.7176	invalid
			2020-juin	2155.5		0.7133	invalid
20	colophony	MGD107	2020-juin	1087.7		0.7114	invalid
	soil	MGD77	2020-juin	1086.20		0.7084	replicable
	pine resin	MGD76	2020-juin	1530.5		0.7102	invalid
6	resin	MGD39R	2020-juin	1008.4		0.7098	invalid
21	colophony	MGD91	2020-juin	2020.0		0.7286	invalid
		MGD90	2020-juin	2009.6		0.7277	invalid
1	colophony	MGD21	9080	2197.35		0.7159	invalid
3	colophony	MGD25	2020-juin	1028.1		0.7123	invalid
26	colophony	MGD103	2020-juin	5177.4		0.7181	invalid
4	linseed oil	MGD30	2020-juin	4179.2		0.7191	invalid

5	linseed oil	MGD31	2020-juin	4102.5		0.7147	invalid
5+3	varnish MGD38+25	MGD45	2020-juin	1199.8		0.7139	invalid
5+1	varnish MGD31+21	MGD47	2020-juin	1226.5		0.7235	invalid
27	turpentine	MGD104	2020-juin	-	5 mL	0.7464	invalid
12	pine resin	MGD54	2020-juin	1053.6		0.7193	invalid
19	pine resin	MGD74	2020-juin	1043.8		0.7103	invalid

6. Isoscape Sr isotope measurements

Table 52. Extracted Sr isotope measurements from isoscapes for comparison

Localisation	Geographical coordinates (Lat./ Long.)	⁸⁷ Sr/ ⁸⁶ Sr ratio	Reference
Avignon	43.847 /4.283	0.7080	Isoscape Sr France - IRHUM
	43.623 /5.492	0.7084	Isoscape Sr France - IRHUM
Besançon	47.307 /6.365	0.7079	Isoscape Sr France - IRHUM
	47.049 /5.357	0.7117	Isoscape Sr France - IRHUM
	46.914 /5.363	0.7135	Isoscape Sr France - IRHUM
Drôme	44.111 /5.944	0.7074	Isoscape Sr France - IRHUM
	44.885 /5.143	0.7080	Isoscape Sr France - IRHUM
	44.892 /5.115	0.7087	Isoscape Sr France - IRHUM
Gascogne	44.296 /-0.025	0.7113	Isoscape Sr France - IRHUM
	44.17 /0.196	0.7142	Isoscape Sr France - IRHUM
Ile-de-France	48.047 /2.622	0.7101	Isoscape Sr France - IRHUM
Landes	44.11 /-0.619	0.7126	Isoscape Sr France - IRHUM
	nd	0.7135	Isoscape Sr France - IRHUM
	44.126 /-1.22	0.7110	Isoscape Sr France - IRHUM
	43.89 /-0.882	0.7127	Isoscape Sr France - IRHUM
Lyon	45.49 /4.994	0.7086	Isoscape Sr France - IRHUM
	45.902 /4.572	0.7103	Isoscape Sr France - IRHUM
	45.756 /4.566	0.7150	Isoscape Sr France - IRHUM

	45.675 /4.527	0.7180	Isoscape Sr France - IRHUM
	45.838 /5.317	0.7090	Isoscape Sr France - IRHUM
Marseille	43.267 /5.741	0.7079	Isoscape Sr France - IRHUM
	43.229 /5.806	0.7079	Isoscape Sr France - IRHUM
Mirecourt	48.252 /6.312	0.7100	Isoscape Sr France - IRHUM
	48.165 /6.869	0.7137	Isoscape Sr France - IRHUM
Saint-Etienne	45.541 /4.446	0.7163	Isoscape Sr France - IRHUM

Appendix 7. PhD activities

1. Curriculum Vitae

Marie-Gabrielle Durier

Physico-chemistry applied to Cultural Heritage materials

Characterisation of inorganic and organic materials

¹⁴C-AMS dating and isotope chemistry

Personal Information

Birth date: July 19, 1990
Place: Brou s/ Chantereine, France
Status: single
Citizenship: French

Home address
21 rue Julien Gudefin
77500 Chelles

Professional addresses (during my PhD)

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Laboratoire de recherche et de restauration
Musée de la musique
ECR team CRC UAR 3224 CNRS
221, avenue Jean Jaurès
75019 Paris cedex
Phone: (+33) 1 44 84 46 95
Email: mgdurier@cite-musique.fr

Scientific Themes

Theme: Material sciences, ¹⁴C geochronology, organic and isotope geochemistry applied to Heritage and archaeological materials.

Research tools: Vis-UV-IR imagery, Optical microscopy, X-Ray Fluorescence, ATR-IRTF, SEM-EDS, GC-MS and ¹⁴C and Sr isotopes on bulk organic matter.

My current objective is to serve historical and/or conservation issues of Cultural Heritage materials as a physical-chemist in an interdisciplinary team, such as in a scientific laboratory within a museum institution. During my Ph.D., I pursued my efforts undertaken since 2014 to develop skills in the characterization of organic and inorganic materials (X-ray diffraction and fluorescence, FTIR, μ Raman, SEM-EDS, GC-MS, etc.), and to meet professionals from different laboratories associated with the same research topic.

Professional / Research Experience

Since Jan. 2019 **Ph.D. student** at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), CEA-CNRS-UVSQ, Gif-sur-Yvette and Laboratoire du musée de la musique, ECR team, CRC USR3224 CNRS.

- Prospection of a corpus of early varnishes and resins/oils. Mechanical sampling on stringed instruments, sleds and furniture from the 17th-18th-19th c. Material characterization of varnishes (Vis-UV-IR, MO, XRF, IRTF-ATR, SEM-EDS, GC-MS).

- Methodological adaptation of ¹⁴C dating to early varnishes of Heritage objects using micro-scalpels for layer by layer sampling (Durier et al. 2021). Experimental reconstruction of early varnishes.
 - Methodological adaptation of Sr isotope analyses for provenance study of organic binders. New protocol to reduce the sample size. Training at ENS Chimie de Rennes (10h).
- Feb. – Dec. 2018 **Young scientist in the Datlm project (DIM-MAP, Ile-de-France) at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), CEA-CNRS-UVSQ, Gif-sur-Yvette and Laboratoire du musée de la musique, ECR team, CRC USR3224 CNRS.**
- Training on chemical protocols and physical measurements for ¹⁴C dating on wooden musical instruments kept at the Musée. Material characterization and sampling: XRF, VIS-UV-IR, OM, ATR-IRTF.
 - Multidisciplinary study with curators. Communication through an article and a poster for the Radiocarbon 2019 conference (Durier et al. 2019).
- Feb. 2017 – Feb. 2018 **Young scientist in the Cordharm project (Labex Patrima, 33 500 € for Cordharm 2) at Laboratoire du musée de la musique, Philharmonie de Paris and CRC USR3224 CNRS in partnership with the Laboratoire Archéomatériaux et Préviation de l'Altération (LAPA) NIMBE CEA-CNRS UMR3685, IRAMAT UMR7065 and Institut de Chimie et des Matériaux Paris-Est, UMR 7182 CNRS, Université Paris-Est Créteil (UPEC).**
- Analyses on 130 piano strings dated from 1780 to 1855: metallography, SEM-EDS, XRD, EPMA. Communication through a presentation and an article during an international conference ICOM METAL 2019 (Durier et al. 2019), shared communication with historians and article in preparation.
- Nov. – Dec. 2015 **Young scientist in the Pleco project at the laboratoire Arc'Antique, Ministère de la culture.**
- 2 weeks to handle a new tool named PLECO and 2 weeks to apply this localized electrochemistry treatment on metallic objects. Writing of machine operating instructions about Pleco and routine protocols for restorers.
- Fev. – Jun. 2015 **Intern scientist at the Royal Institute for Cultural Heritage (KIK-IRPA, Brussels).**
- Countless samples of crushed bricks contaminated with salts (Na₂SO₄) analysed using HPLC ion chromatography. Raman microanalyses on a hundred samples of the geology department at the Royal Belgian Institute of Natural Sciences (Brussels) registered in a database.
- Av. – Jun. 2014 **Intern scientist at the European Archaeometry Centre and Institut de Physique Nucleaire, Atomique (IPNAS) (University of Liège)**
- In-situ* characterization of the pigments of paintings (Gauguin, Chagall, Picasso...) using a mobile laboratory: X-ray fluorescence, Raman spectrometry, UV fluorescence and IR reflectance. Bibliographical study on pigments used by painters before/after 1850 with an art historian.

Qualifications

Scientific education

- 2019-2021 **Ph.D. in Physics**, (Fondation des Sciences du Patrimoine, ED129, University of Versailles Saint-Quentin-en-Yvelines) Thesis title: " Contribution of geochemistry and geochronology to the knowledge of the history of the uses of modern musical instruments". Advisor: Dr Christine Hatté.
- 2014-2015 **Master in Environment** and Cultural Heritage materials, University of Créteil Paris XII. Master Thesis Translated title: "Evaluating the effects of a salt extraction poultice on different substrates". Advisor: Sebastiaan Godts (KIK-IRPA, Brussels)

- 2013-2014 Master in Physics (University of Sorbonne Paris VI Pierre and Marie Curie) Master Thesis
Translated title: "Non-destructive analyses of the modern art paintings of the Musée de
Beaux-Arts de Liège". Advisor: Dr. David Strivay.
- 2010-2013 Bachelor in Physical Sciences, (University of Paris Est Marne-la-Vallée) Environment,
Physics, Chemistry, Instrumentation. Major in Physics-chemistry (ranked 1st out of 17).

Artistic education

- 2008-2010 Architecture School (Ecole d'Architecture de la Ville et du Territoire) Software skills
using Autocad, Photoshop, Illustrator, Indesign, Sketchup

Teaching interests

- 2021 Tutoring of third-year Bachelor of Science students on a project study. Translated title:
"Radiocarbon ¹⁴C to date a Chinese *qin*"
- 2019 54h of teaching in French Universities (University of UVSQ and Orsay) in Electrokinetics,
Optics, Mechanics for first-year Bachelor of Science students

Extraprofessional experience

- 2019-2021 Copies of early paintings at the Atelier Vermeer, Paris.
- 2019-2020 Logistics manager in the Public speaking association Toastmaster Les Ailes, Paris
- 2013-2016 Private tutor in physics-chemistry-math
- 2010 Volunteer in the CMV association for the restoration of a medieval abbey
- Sports activities Ballet (8 years), Aïkido (3 years)

2. Communications

Peer-Reviewed Journals

- Durier, M.-G., Girard-Muscagorry, A., Hatté, C., Fabris, T., Foasso, C., Nowik, W., & Vaiedelich, S. (2021). The story of the "Qiuilai" qin unraveled by radiocarbon dating, Chinese inscriptions and material characterization. *Heritage Science*, 9(1), 89. <https://doi.org/10.1186/s40494-021-00563-8>
- Durier, M.-G., Bruguère, P., Hatté, C., Vaiedelich, S., Gauthier, C., Thil, F., & Tisnérat-Laborde, N. (2019). Radiocarbon dating of legacy music instrument collections: Example of a traditional Indian vina from the Musée de la musique, Paris. *Radiocarbon*, 61(5), 1357–1366. <https://doi.org/10.1017/RDC.2019.71>
- Durier, M. G., Villiaume, L., Pires, R., Cotrebil, Y., Vega, E., Houssay, A., Battault, J.-C., Vion, M., Clarke, C., Guillot, I., Dillmann, P., & Vaiedelich, S. (2019). Iron Piano Wire Production at the Beginning of the 19th c. *Metal 2019 Proceedings of the Interim Meeting of the ICOM-CC Metals Working Group*, 49–57. <https://www.icom-cc-publications-online.org/3561/Iron-piano-wires-production-at-the-beginning-of-the-nineteenth-c.--an-interdisciplinary-study-from-Techniques-History-to-Material-Sciences>
- Durier, M.-G., Guillot, I., Dillmann, P., & Vaiedelich, S. (in preparation). Characterization of iron piano wires at the beginning of the nineteenth century. *Materials Characterization*.

International Conferences

Oral presentation

Durier, M.-G., Vaiedelich, S., Dillmann, P., & Guillot, I. (2021, October 27). La production des cordes de piano au début du 19ème siècle. SF2M 2021 Journées Annuelles Société Française de Métallurgie et de Matériaux.

Durier, M.-G., Hatté, C., Vaiedelich, S., Gauthier, C., Noury, C., Thil, F., Tisnérat-Laborde, N., Bruguière, P., Echard, J.-P., & Laloue, C. (2018, November 27). Radiocarbon dating application to modern musical instruments: An interdisciplinary study. 6ème Journée REFRAIN.

Durier, M.-G., Hatté, C., Vaiedelich, S., Gauthier, C., Noury, C., Thil, F., Tisnérat-Laborde, N., Bruguière, P., Echard, J.-P., & Laloue, C. (2018, November). Radiocarbon dating application to modern musical instruments: An interdisciplinary study. Labs, Art and Relics.

Poster

Durier, M.-G., Hatté, C., Vaiedelich, S., Gauthier, C., Noury, C., Thil, F., Tisnérat-Laborde, N., Bruguière, P., Echard, J.-P., & Laloue, C. (2018, June 17). Radiocarbon dating application to modern musical instruments: An interdisciplinary study. 23rd International Radiocarbon Conference.

Shared Conferences

Oral presentation

Vaiedelich, S., Durier, M.-G., & Hatté, C. (2018, October 1). Inventer le violoncelle, histoire d'une transformation, le moule E. 901.1 attribué à A. Stradivari. Congrès International de l'EIEL.

Durier, M.-G., & Villiaume, L. (2017, June 30). L'étude de la fabrication des cordes harmoniques de piano: Une collaboration nécessaire entre l'histoire des techniques et la science des matériaux. Journée d'études de La Fondation Des Sciences Du Patrimoine.

Scientific Mediation

Hatté, C., & Durier, M.-G. Des cithares patrimoniales indiennes datées au carbone 14. Site de La Direction Des Sciences Du Vivant Du CEA. <http://www.cea.fr/drf/Pages/Actualites/En-direct-des-labos/2019/des-cithares-patrimoniales-indiennes-datees-au-carbone-.aspx>

Mathieu, A., Durier, M.-G., & Hatté, C. La petite musique interne du qin qiulai enfin révélée: Quand la science compose. Site Actualités Université Paris-Saclay. <https://news.universite-paris-saclay.fr/actualites/la-petite-musique-interne-du-qin-qiulai-enfin-revelee-quand-la-science-compose>

2.1. Poster

Carbon-14 dating application to modern musical instruments: an interdisciplinary study

M.-G. Durier^{1,2}, C. Hatté², S. Vaiedelich¹, C. Gauthier², F. Thil², N. Tisnérat-Laborde², P. Bruguère¹, J.-P. Echard¹, C. Laloue¹

¹ECR-Musée de la musique-USR3224 CRC, Paris, France

²LSCE-UMR 8212 CEA-CNRS-UVSQ, Université Paris-Saclay, 91198 Gif-sur-Yvette, France



Museum context and objectives



The first two analysed vinas: (right) Indian rudra-vina E.997.24.1. (left) kinnari-vina, E.1444 from the Musée de la musique collections.



(left to right) Vielle Sarangi, E.1403 (India). Lute Tambura, D.973.6.2 (South India). Non inventoried broken bow, 6D. From the Musée de la musique collections.



Harpsichord, E.233 Jean-Claude Goujon / Jacques Joachim Sassen from the Musée de la musique collections.

Besides a variety of classical analysis methods used in cultural heritage institutions, this research applies radiocarbon dating to deepen our scientific knowledge of the "restoration history" of instruments and to understand their use since they emerged from instrument factories.

Within the DATim project, our team studied several corpora: 17th century violin bows and their successive musical practices; harpsichords and their elements that have been renovated over time.

Here, we present the first results obtained by combining historical evidence and fine radiocarbon dating on 2 Indian vinas of unknown age and 2 emblematic lutes of the 16th or the 17th centuries.

Experimental process

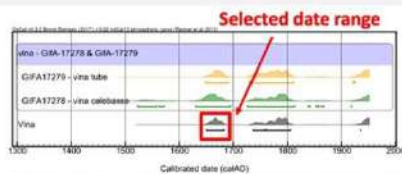
There has been only one ¹⁴C study on instruments manufactured during the Modern period, i.e. between the 16th and the 19th century (Chase et al. 2009, Jew.Hist.St.), as there are three challenges to face: i- the sample size, which cannot exceed a few hundred micrograms, ii- the composite constitution of the instrument (varnishes, glues, restored parts), which requires specific and complex chemical protocols and iii- the historical period which is unfavorable to radiocarbon dating (Reimer et al. 2013 Radiocarbon). To overcome these challenges, our research program combined the expertise of the museum conservators at the Musée de la Musique, appropriate chemical treatments of the selected samples and recent technological advances in radiocarbon dating.

(Left to right) 1- Sampling by a curator. 2- Protocol of chemical treatments suited to each sample for removing traces of glue, varnishes, dyes, etc. 3- Samples are burned to produce a carbon gas. 4- The mass spectrometer ECHOmicADAS quantifies the ¹⁴C activity in each sample (gas source).



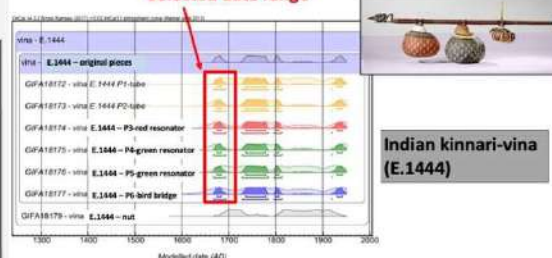
Results

Indian rudra-vina (E.997.24.1)



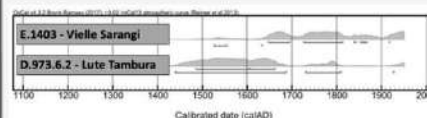
Transcription of ¹⁴C activity measured on two sub-samples yields four equiprobable calibrated date ranges. The comparison with Govardhan's pictorial representation of a similar rudra-vina made it possible to determine the most likely date range: [AD 1650-1683].

Selected date range



Indian kinnari-vina (E.1444)

The dating, based on 7 sub-samples, evidenced a very likely restoration of the nut (GIFA18179-vina E.1444 nut) whereas all the other components are contemporaneous of the instrument manufacturing. The most likely date range was defined statistically: [AD 1675-1683]



Ages of a sarangi and a tambura were assigned to the first and the second half of the 17th century, respectively.

2.2. Dissemination activities

Participation in the "Learning Center" project to promote portraits of Ph.D students of the university Paris-Saclay. The art-science project developed by the laboratoire de recherche en informatique (LRI) with a professional photographer (Didier Goupy) consists in a dynamic and interactive presentation of these portraits to the general public for example during graduation ceremonies (e.g. June 2019) or Science Festivals (e.g. Gif-sur-Yvette, October 2019) (Figure 142). Visitors can manipulate the interface and discover their different research topics. The digital platform will be on permanent display in the future Learning Center of the Université Paris-Saclay. The portraits of Ph.D students will be eventually added to the website of Paris-Saclay in the same way as current portraits of researchers:

<https://www.universite-paris-saclay.fr/en/research/researcher-portraits>



Figure 142. interactive presentation of portraits of Ph.D students of the university of Paris-Saclay to the general public during the Science Festival, Gif-sur-Yvette, Ferme du Moulon, 5-6th October 2019.

<https://mediatheque.universite-paris-saclay.fr/s/mediatheque/item/81176#c=&m=&s=&cv=&xywh=-10660%2C-1%2C27319%2C6000>

RADIOCARBON DATING OF LEGACY MUSIC INSTRUMENT COLLECTIONS: EXAMPLE OF TRADITIONAL INDIAN *VINA* FROM THE MUSÉE DE LA MUSIQUE, PARIS

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ABSTRACT. Although radiocarbon (¹⁴C) dating is commonly used for archeological music instruments, little research has been conducted on modern instruments (16th–19th centuries). New technology, based on the Mini Carbon Dating System (MICADAS), enables some of the recurring challenges (e.g. sampling size) to be circumvented and paves the way for a new field of investigation. We here address the Indian instrumentarium, about which very little is known. We investigate the making and the restoration phases of two *vina*, a *kinnari vina* (E.1444), and a *rudra vina* or *bin* (E.997.24.1). By comparing ¹⁴C measurements made on several samplings of elements of the instruments with museological information, we were able to specify a unique calibrated interval of ages [1666 AD–1690 AD] for the *kinnari vina*, with a restoration phase [1678 AD–1766 AD] for the upper nut. The *bin* is likely attributed to the [1650 AD–1683 AD] interval.

KEYWORDS: ¹⁴C dating, modern musical instrument, small sample.

INTRODUCTION

Several challenges have to be met concerning the radiocarbon (¹⁴C) dating of modern music instruments made between the 16th and 19th centuries. Dendrochronology cannot be carried out on modern music instruments as the tree-ring record is too short and ¹⁴C dating may be a priori rejected for historical periods as a ¹⁴C physical measurement may result in several equiprobable age ranges. Several samplings and independent expertise are then required to make a well-considered choice between these intervals. Owing to the new generation of ¹⁴C dating instruments, a compact ¹⁴C dating system such as the Mini Carbon Dating System (MICADAS) (Synal et al. 2007) allows some hundreds of micrograms of material to be sampled. For wood, the sample is thus as small as a pinhead. This new technology opens the door to multisampling without it being visible and without it affecting the instrument's playing quality. This might at least partly resolve issues of multi-interval calibration. Beyond the physical analysis, museum studies are another reliable means of investigation to attempt to find clues to the manufacturing period and history of the instrument. This approach involves the gathering of documents, the expertise of curators and restorers, and reports of scientific analyses used in cultural heritage institutions that are required for the study of instruments using ¹⁴C dating. The interdisciplinary framework makes it possible to combine any *ante quem* or *post quem* information on the age of relics or music instruments. In this approach, we will draw on an ongoing project on modern music instruments involving radiocarbon dating specialists and museum experts. There are three challenges to be overcome: (1) the sample size, which will not extend beyond a few hundred micrograms, (2) the composite constitution of the instrument (varnishes, glues, restored parts), which requires specific and complex chemical protocols to extract the

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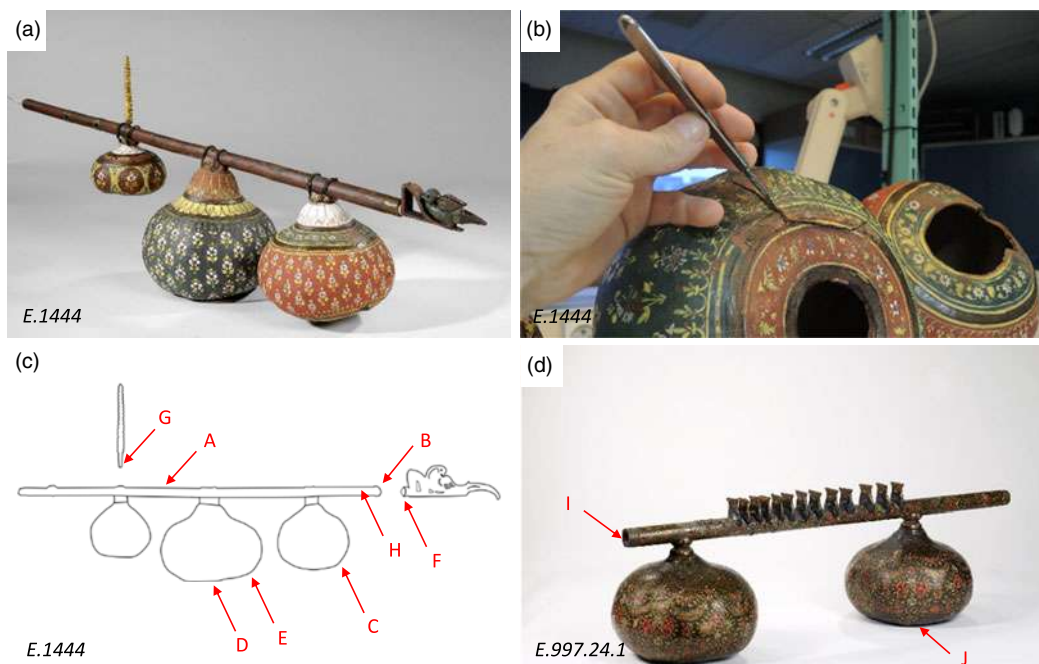


Figure 1 Indian *vina* from the museum collections and sampling locations: (a) *kinnari vina* E.1444, (b) close up of sampling in a crack from *kinnari vina* E.1444, (c) schematic view of the *kinnari vina* E.1444 and location of the 8 samples, (d) *bin* or *rudra vina* E.997.24.1 and sample locations. Pictures by Claude Germain (a, d) and Stéphane Vaiedelich (b) © Musée de la musique-Philharmonie de Paris.

carbon to be dated, and (3) the historical period which is not favorable to radiocarbon dating due to complex calibration curves. Our goal here is to date two amazingly well-preserved *vina* about which little information is available and possibly contribute to scientific knowledge about their origin and the history of their making.

MATERIAL AND METHOD

Material

Our study focuses on two *vina*, Indian stringed instruments belonging to the tube zither family and kept at the Musée de la musique in Paris. The first one is a *kinnari vina* (E.1444, Figure 1a,b). The second one is a *bin* (also called today *rudra vina*) (E.997.24.1, Figure 1d), which was played for centuries in North Indian princely courts. *Vina* are composed of a wooden tube onto which are fixed gourds which act as resonators. The conservation state of both *vina* is exceptional, although the constitutive and painted parts are very fragile and the storage conditions under the initial tropical climate were unfavorable, according to museum studies. Visual inspections under an optical microscope, endoscopic analysis, x-ray digital radiography, and XRF investigations were performed during museum studies and showed no visible evidence to suspect that certain parts had been replaced. None of the *vina* showed visible surface contamination. The decorations are original and it is very likely that gourds were chosen with care according to their acoustic properties (Bruguière et al. 2008).

The *kinnari vina* (E.1444, **Figure 1a,b**) is made of three gourds (*Lagenaria siceraria*) fixed under a reed tube, made of *Arundo donax*, a species found in East and Southeast Asia. This makes this *kinnari vina* singular. A piece of wood from a *Dalbergia latifolia*, named “Indian rosewood,” was carved in the form of a bird (a parrot) and inserted at the end of the tube. This part was used as a string holder and a bridge. The upper nut painted yellow with orpiment is made of *Artocarpus chama* Buch, a wood commonly called “terap” and found in Southeast Asia. An ancient iconography (Day 1891) presents a *kinnari vina* showing the same singular features without any decoration. The *kinnari vina* E.1444 entered the collections in 1892. It was sold to the museum by Gand and Bernardel, renowned Parisian violin makers and valuable music instrument dealers of the 19th century, who may have bought it in a public sale. The floral pattern of this *kinnari vina* is a motif found on 17th and 18th century artifacts produced in the region of Hyderabad (Andhra Pradesh) situated in Southeast India. According to the curator who relies on organological features and the painted patterns, this musical instrument could have been made in the 18th century.

The *bin* or *rudra vina* (E.997.24.1, **Figure 1d**) consists of two resonators made of gourds, a tube made of teak wood (*Tectona grandis*), and 13 wooden frets. The pegs and the string holder are missing. A mixture of beeswax and plant resin was traditionally used to stick the frets onto the tube. The highly sophisticated decoration of this *vina* comprises five successive layers: an undercoat of clay with iron oxides, a support of metallic sheet in tin, an organic layer with resin and paint layers. This *bin* was acquired by the museum in 1997. It is referenced as coming from Rajasthan, Northwest India, and it has been tentatively dated from the first half of the 17th century.

Method

Sampling

The ^{14}C activity was measured on 7 subsamples, representative of each of the constituent elements, of the *kinnari vina* (**Figure 1c**, **Table 1**) and on two subsamples of the *bin* (**Figure 1d**, **Table 1**). An eighth sample was taken on the *kinnari vina*: a black glue residue found inside the tube (**Figure 1c**, sample H). All the samples were of less than a few hundred micrograms of carbon. Samples taken from both *vina* belong to original components of the instruments. Each of them is devoid of any traces of varnish, painting, and wax and protected from other environmental contamination. They were taken in nonvisible areas inside the gourds or the tube, inside cracks, etc. (**Figure 1b**).

Treatment

As no visible surface contamination was highlighted through previous investigations and samples were extracted from hidden, uncolored parts of the instruments, a simple chemical treatment was enough to prepare the samples for ^{14}C dating.

The samples were treated with the classical AAA chemical pretreatment for wood and charcoal samples (Van Klinken and Hedges 1998). All chemicals were of ultrapure quality, and water was ultrapure (MilliQ grade). Chemical glasses were pre-combusted at 500°C overnight prior to use and were preserved in Al foil (burnt at the same time). The procedure is as follows:

HCl 0.5M, ambient temperature, sample is rinsed until $\text{pH} = 5$

NaOH 0.1M, ambient temperature, sample is rinsed with hot water until pH = 5 (80°C)

HCl 0.5M, ambient temperature, sample is rinsed until pH = 5

Clean samples were transformed into CO₂ by flame-combustion with pure O₂. Evolved gases were passed through a trap kept at -80°C (ethanol-dry ice mixture) and on Cu/Ag to get rid of water, O₂ excess and sulfur and nitrogen oxides. The amount of pure carbon was evaluated by a pressure transducer. Pure CO₂ was then flame-sealed, under vacuum, in one or several Pyrex tubes until measurement. No more than 140 µg of C were preserved per tube.

To control the impact of chemical treatment and of the combustion, we also ran “blank” and international standards (SIRI G—Scott et al. 2017). As a “blank,” we used a F¹⁴C=0 charcoal, known as “Afrique du Sud,” from inside the Border cave (South Africa) in a Paleolithic level (Middle Stone Age) dated to more than 70 kya.

Physical Measurements

The mass spectrometer *ECHO*MICADAS (¹⁴C AMS) was used to measure the ¹⁴C activity of each sample (Synal et al. 2007; Tisnérat-Laborde et al. 2015). The gaseous samples (from 30 to 140 µgC) were directly injected into the MICADAS gas source through the gas ion source interface (GIS) (Ruff et al. 2010) by tube cracking. Ages were obtained from ¹⁴C measurements using Bats software by comparing ¹⁴C/¹²C ratios with OXII standards (Wacker et al. 2010). Most of the samples provided several tubes of gas. All the tubes were separately measured, but results were statistically combined. The mean age of the sample then derives from the mean of the individual measurements, which pass the Chi² test, and is associated to the maximum between the Chi² reduced error and the standard deviation between the median of the individual measurements. Results are expressed in F¹⁴C as recommended by Reimer et al. (2004) and provided as ¹⁴C ages (yr BP) following Stuiver and Polach’s (1977) convention. Probability distributions of calibrated ¹⁴C ages were

Table 1 List of samples from *kinnari vina* and *rudra vina* (refer to Figure 1 for locations).

Vina #	Sampling #	GifA #	Sampling description
Kinnari-vina E.1444	A	GifA18172	Inside the central part of the tube in the thickness of a crack
	B	GifA18173	Inside the end of the tube on the bird bridge side
	C	GifA18174	In the thickness of a broken part of the red gourd
	D	GifA18175	On the inner surface of the green gourd
	E	GifA18176	Inside a crack of the green gourd
	F	GifA18177	Part of the bird bridge that fits into the end of the tube
	G	GifA18179	Part of the upper nut that fits into the tube
	H	GifA18178	Black glue-like residue from inside the tube
Rudra-vina E.997.24.1	I	GifA17279	Inside the tube
	J	GifA17278	Under a gourd

generated using OxCal v4.3.2 (Bronk Ramsey 2009) based on the IntCal13 calibration curve (Reimer et al. 2013). All data are provided in Tables 1 and 2.

RESULTS AND DISCUSSION

Vina resonators are made of gourds that are fast growing and quickly dried plants. The same is true for the reed used as the tube for the *kinnari vina*. This means that the ^{14}C dating will correspond to the year of manufacture to the nearest 1 to 3 years. The *rudra vina* tube, in contrast, is made of teak that is either a fast or a slow growing species depending on the environment. Examination of the tube revealed that it cannot have come from a branch but from a piece of turned wood. It comes from a beam that was drilled all along its length. We do not know *a priori* if it was extracted from the external part (the youngest part) or from the internal part (the oldest part) of the tree.

Kinnari Vina (E 1444)

^{14}C data obtained for each sample are shown in Table 2 and Figure 2. The F^{14}C data recorded for six samples (GifA18172 to GifA18177) were unexpectedly very similar: 0.983 ± 0.005 (GifA18172), 0.977 ± 0.005 (GifA18173), 0.977 ± 0.005 (GifA18174), 0.977 ± 0.006 (GifA18175), 0.977 ± 0.005 (GifA18176), 0.982 ± 0.007 (GifA18176), 0.977 ± 0.009 (GifA18177). Hence, they correspond respectively to similar ^{14}C dates: 135 ± 40 yr BP, 190 ± 40 yr BP, 190 ± 50 yr BP, 190 ± 45 yr BP, 150 ± 55 yr BP, 190 ± 75 yr BP. This result supports the conclusions of the museum studies that these pieces are original, and therefore correspond to the period when the instrument was made. The result for the upper nut (GifA18179) is an exception: 0.986 ± 0.005 , i.e., a ^{14}C date of 115 ± 40 yr BP. Unlike the first investigations carried out in the laboratory of the Musée de la Musique, this piece does not seem to be original.

Combining the results of this series (7 samples) using the “combine” option of Bayesian modeling (Bronk Ramsey 2009) shows that the individual agreement index (A) for the upper nut sample (GifA18179) is 60.4% whereas it is between 90 and 125% for the other six samples. It was therefore decided to perform the Bayesian modelling without the nut, i.e. using only the six subsamples labeled GifA18172 to GifA18177 (Tables 1 and 2). The resulting equiprobable calendar ranges are (Figure 2, Table 2): [1666 AD–1690 AD] (17.8%), [1730 AD–1784 AD] (49.8%), [1796 AD–1810 AD] (9.9%) (the last one, [1926 AD–...] is outlier data due to the Suess effect). The three main ranges of calibrated dates are defined as the end of the 17th century and the 18th century.

As mentioned above, the upper nut may not be contemporaneous of the *vina* manufacture. It could be a replacement of the original nut that was probably lost or broken. This fragile part is subject to breakage and was likely changed during the period when the *vina* was played. The main probable ranges for the upper nut are: [1678 AD–1766 AD] (32.5%), [1772 AD–1778 AD] (1.0%), [1800 AD–1941 AD] (61.9%).

The instrument was acquired in 1892 and no restoration has been carried out since it entered the museum. Any replacement was thus done before. The use of terap in 19th-century Europe in cabinet making and instrument making is not attested and remains highly unlikely. European instrument makers of this era probably did not have the organological knowledge of traditional Indian instruments to accurately reproduce this part, either. It is very likely that the replacement was done while the instrument was still in India and was

Table 2 Conventional, calibrated and modeled ¹⁴C ages obtained for the kinnari vina E.1444. Statistical results of Bayesian modeling are shown in the last four columns: for all vina pieces first and for the original pieces of the vina thereafter. Individual agreement (Aind) and combined agreement (Acomb) are provided. Resulting modeling intervals are provided under the main part of the table.

identification				uncalibrated data						calibrated age [1]		statistical combination				
				individual measurement		Chi2-Test (5%)	mean value					model 1 (A->G) [2]		model 2 (A-> F) [3]		
Sample ID	Fig.1 ID	GifA #	ECHO #	F ¹⁴ C	±		F ¹⁴ C	±	age BP [yr]	±	calibrated age (± 1 s) [range in yr] (probability distribution)	calibrated age (± 2 s) [range yr] (probability distribution)	A _{ind}	A _{comb}	A _{ind}	A _{comb}
vina E1444 - P1 tube	A	GifA - 18172	ECHO - 2353	0.983	0.007	0.21/3.84	0.983	0.005	135	40	[1680 - 1700] (8.9%) [1703 - 1707] (1.6%) [1720 - 1764] (18.0%) [1801 - 1819] (7.8%) [1824 - 1825] (0.2%) [1833 - 1881] (20.8%) [1915 - 1939] (10.7%)	[1669 - 1781] (41.7%) [1798 - 1894] (38.2%) [1905 - 1946] (15.6%)	99.1		89.8	
				0.984	0.007		0.977	0.005	190	40	[1663 - 1683] (13.6%) [1736 - 1806] (43.4%) [1931 - 1933] (0.7%) [1935 - ...] (10.5%)	[1645 - 1699] (22.7%) [1722 - 1817] (49.8%) [1834 - 1880] (6.6%) [1916 - ...] (16.4%)				
vina E1444 - P2 tube	B	GifA - 18173	ECHO - 2354	0.9738	0.0066	0.37/3.84	0.977	0.005	190	40	[1653 - 1690] (16.7%) [1730 - 1810] (39.6%) [1926 - ...] (11.9%)	[1644 - 1712] (22.7%) [1719 - 1830] (45.2%) [1831 - 1891] (11.9%) [1909 - ...] (15.5%)	106.4		116.4	
				0.9797	0.0070		-	0.977	0.006	190	50	[1660 - 1685] (14.0%) [1733 - 1808] (41.8%) [1929 - ...] (12.4%)				
vina E1444 - P3 red resonator	C	GifA - 18174	ECHO - 2355	0.9768	0.0062	-	0.977	0.006	190	50	[1669 - 1698] (11.2%) [1724 - 1781] (22.8%) [1798 - 1816] (6.9%) [1835 - 1878] (15.8%) [1917 - 1946] (11.5%)	[1665 - 1788] (44.5%) [1790 - 1895] (34.6%) [1904 - ...] (16.3%)	119.8		126.5	
				0.9795	0.0077	0.28/3.84	0.977	0.005	190	45	[1647 - 1696] (16.8%) [1726 - 1814] (32.4%) [1837 - 1844] (2.0%) [1852 - 1869] (4.4%) [1872 - 1877] (1.1%) [1918 - ...] (11.5%)	[1523 - 1575] (5.0%) [1629 - ...] (90.4%)				
vina E1444 - P4 green resonator	D	GifA - 18175	ECHO - 2356	0.9739	0.0076	-	0.977	0.005	190	45	[1690 - 1730] (19.3%) [1810 - 1892] (40.4%) [1908 - 1926] (8.5%)	[1678 - 1766] (32.5%) [1772 - 1778] (1.0%) [1800 - 1941] (61.9%)	113.5	109.4	121.9	142.1
				0.9739	0.0076	-	0.977	0.005	190	45	[1669 - 1698] (11.2%) [1724 - 1781] (22.8%) [1798 - 1816] (6.9%) [1835 - 1878] (15.8%) [1917 - 1946] (11.5%)	[1665 - 1788] (44.5%) [1790 - 1895] (34.6%) [1904 - ...] (16.3%)				
vina E1444 - P5 green resonator	E	GifA18176	ECHO-2357	0.9816	0.0066	-	0.982	0.007	150	55	[1647 - 1696] (16.8%) [1726 - 1814] (32.4%) [1837 - 1844] (2.0%) [1852 - 1869] (4.4%) [1872 - 1877] (1.1%) [1918 - ...] (11.5%)	[1665 - 1788] (44.5%) [1790 - 1895] (34.6%) [1904 - ...] (16.3%)	115.3		111.9	
				0.9766	0.0088	-	0.977	0.009	190	75	[1647 - 1696] (16.8%) [1726 - 1814] (32.4%) [1837 - 1844] (2.0%) [1852 - 1869] (4.4%) [1872 - 1877] (1.1%) [1918 - ...] (11.5%)	[1523 - 1575] (5.0%) [1629 - ...] (90.4%)				
vina E1444 - P6 bird bridge	F	GifA18177	ECHO-2358	0.9766	0.0088	-	0.977	0.009	190	75	[1690 - 1730] (19.3%) [1810 - 1892] (40.4%) [1908 - 1926] (8.5%)	[1678 - 1766] (32.5%) [1772 - 1778] (1.0%) [1800 - 1941] (61.9%)	127.1		131.2	
				0.9766	0.0088	-	0.977	0.009	190	75	[1690 - 1730] (19.3%) [1810 - 1892] (40.4%) [1908 - 1926] (8.5%)	[1678 - 1766] (32.5%) [1772 - 1778] (1.0%) [1800 - 1941] (61.9%)				
vina E1444 upper nut	G	GifA18179	ECHO-2360	0.9864	0.0064	0.01/3.84	0.986	0.005	115	40	[1669 - 1698] (11.2%) [1724 - 1781] (22.8%) [1798 - 1816] (6.9%) [1835 - 1878] (15.8%) [1917 - 1946] (11.5%)	[1665 - 1788] (44.5%) [1790 - 1895] (34.6%) [1904 - ...] (16.3%)	60.3			
				0.9855	0.0073		-	0.977	0.007	1820	65	[1669 - 1698] (11.2%) [1724 - 1781] (22.8%) [1798 - 1816] (6.9%) [1835 - 1878] (15.8%) [1917 - 1946] (11.5%)				
vina E1444 - P7 inner tube deposit	H	GifA18178	ECHO-2359	0.7973	0.0066	-	0.797	0.007	1820	65	[1669 - 1698] (11.2%) [1724 - 1781] (22.8%) [1798 - 1816] (6.9%) [1835 - 1878] (15.8%) [1917 - 1946] (11.5%)	[1665 - 1788] (44.5%) [1790 - 1895] (34.6%) [1904 - ...] (16.3%)	resulting calibrated age (± 2 s) [1668 - 1693] (16.2%) [1666 - 1690] (17.8%) [1728 - 1782] (49.7%) [1730 - 1784] (49.8%) [1798 - 1812] (10.7%) [1796 - 1810] (9.9%) [1920 - 1949] (18.7%) [1928 - ...] (18.0%)			

[1] using OxCal4.3.2 (Bronk Ramsey 2009) based on IntCal13 (Reimer et al. 2013)

[2] Chi2-Test: T= 3.30/12.59 (5%)

[3] Chi2-Test: T=1.54/11.07 (5%)

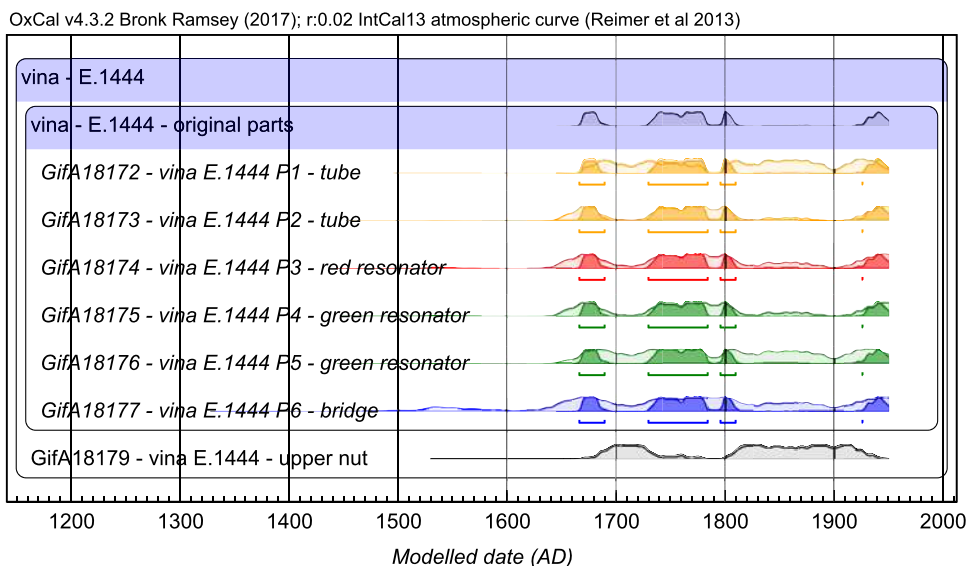


Figure 2 Calibrated ^{14}C ages of the *kinnari vina* E.1444. The upper probability distribution diagram, underlined in blue corresponds to the Bayesian modeling of the combination of the *vina*'s original parts. The probability distribution diagram of the restored piece (upper nut) is shown in the last line.

made by an Indian instrument maker. The only few slight traces of (musical) use on the upper nut seem to reveal that it was not played as much as the other parts of the *vina*. It is thus assumed that the nut was replaced during the [1678 AD–1766 AD] interval, towards the end of the musical use of the *vina*. Consequently, the instrument was made (age of the original pieces) during the [1666 AD–1690 AD] interval. It appears that the instrument is a little older than initially thought by the curator, who expected it to date from the 18th century.

Residue sampled in the *vina* tube shows quite different results, with $F^{14}\text{C}$ equal to 0.797 ± 0.007 , equivalent to an age of 1820 ± 65 BP (Table 2). Chemical characterization (chromatography, XRF...) of a new sample of the same black residue is in progress. It is known that bitumen-derived glue was used to maintain the tube when aligning elements and perforating holes. A balance equation between expected age ($F^{14}\text{C} = 0.979$, the modeled average of original pieces' $F^{14}\text{C}$) and a null ^{14}C content for a potential bitumen-derived component would result in a mixture containing about 20% of dead carbon in the resulting black residue, which is quite likely.

Rudra Vina (E 997.24.1)

^{14}C data obtained for each sample are shown in Table 3. Samples from the *vina* tube (GifA-17279) and the *vina* resonator (GifA-17280) provided very similar $F^{14}\text{C}$ data: 0.976 ± 0.004 and 0.973 ± 0.005 , respectively, equivalent to 195 ± 30 yr BP and 225 ± 40 yr BP, respectively. Calibrated ranges of dates of both samples are thus also very close (Table 3 and Figure 3) yielding three major ranges of dates, during the 17th century, the 18th century and associated to the Suess effect modern period. This concomitance of ages reveals that the tube was extracted from the external part of the tree and this allows Bayesian modeling to combine dating and reduce uncertainties.

Table 3 Conventional, calibrated, and modeled ¹⁴C ages obtained for the bin E.997.24.1. Statistical results of Bayesian modeling are shown in the last two columns. Individual agreement (A_{ind}) and combined agreement (A_{comb}) are provided. Resulting modeling intervals are provided under the main part of the table.

identification				uncalibrated data				calibrated age [1]		statistical combination [2]				
Sample ID	Fig.1 ID	GifA #	ECHO #	individual measurement		Chi-Test (5%)	mean value				calibrated age (±1 sigma) [range in yr AD] (probability distribution)	calibrated age (±2 sigma) [range yr AD] (probability distribution)	A _{ind}	A _{comb}
				F ¹⁴ C	±		F ¹⁴ C	±	age BP [yr]	±				
vina E997.24.1 tube	I	GifA - 17279	ECHO - 1938	0.979	0.007	0.57/5.99	0.976	0.004	195	30	[1663 - 1681](16.2%)	[1649 - 1691](23.9%)	111.7	120.7
				0.973	0.006						[1739 - 1746](4.9%)	[1729 - 1811](54.8%)		
				0.977	0.006						[1748 - 1751](1.9%)	[1921 - 1923](0.2%)		
				0.972	0.007					[1763 - 1802](33.5%)	[1925 - 1951](16.6%)			
										[1938 - 1950](11.7%)	[1524 - 1559](4.1%)			
										[1644 - 1681](29.8%)	[1563 - 1571](0.4%)			
										[1631 - 1695](34.5%)	[1631 - 1695](34.5%)			
vina E997.24.1 resonator	J	GifA - 17278	ECHO - 1939			0.007/3.84	0.973	0.005	225	40	[1740 - 1742](1.0%)	[1727 - 1813](43.4%)	116.9	
											[1764 - 1801](29.2%)	[1838 - 1842](0.2%)		
											[1939 - 1950](8.3%)	[1854 - 1858](0.2%)		
				0.973	0.007					[1862 - 1867](0.2%)	[1920 - 1950](12.2%)			
resulting calibrated age (±2 s)												[1650 - 1683](27.9%)		
[range yr] (probability distribution)												[1736 - 1759](9.4%)		
												[1760 - 1805](43.6%)		
												[1935 - 1951](14.5%)		

[1] using OxCal4.3.2 (Bronk Ramsey 2009) based on IntCal13 (Reimer et al. 2013)

[2] Chi-Test: T= 0.30/3.84 (5%)

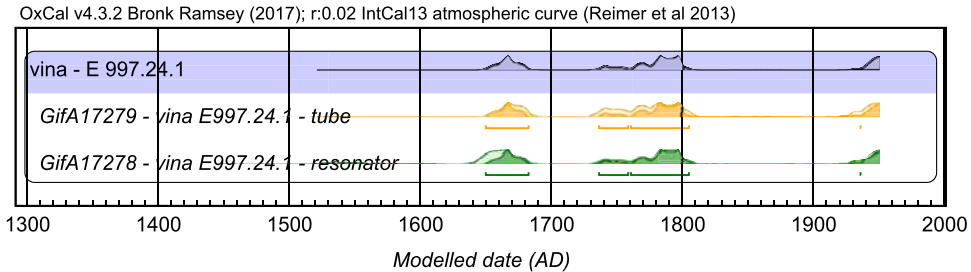


Figure 3 Calibrated ^{14}C ages for the two gaseous micro-samples from the *bin* or *rudra vina* E.997.24.1. The upper probability distribution diagram, underlined in blue, corresponds to the Bayesian modeling obtained by combination of bin ^{14}C results. (Please see electronic version for color figures.)

Bayesian modeling with OxCal (Bronk Ramsey 2009) reinforced the view that the two elements were associated at the same time and thus very likely correspond to the making of the instrument (Figure 3). Individual agreements, A , are 111.7% and 116.9%, respectively, resulting in a combined agreement factor of $A_{\text{comb}} = 120.7\%$. Modeling results in four equiprobable ranges of dates: [1650 AD–1683 AD] (28.1%), [1737 AD–1759 AD] (8.8%), and [1761 AD–1805 AD] (43.9%) and the last one ([1936 AD–...] corresponding to the modern period that we ruled out.

According to the very accurate iconographical evidence and descriptions given in textual sources dating from the end of the 16th century and early 17th century, the curator speculated that the *vina* could have been made in the first half of the 17th century. The [1650 AD–1683 AD] interval is presumably that when the instrument was made. This interval is slightly more recent than expected.

CONCLUSION

Based on information from both geochronological analyses and museological resources, we were able to provide key elements on two *vina* from the Musée de la Musique. The making of the *rudra vina* E.997.24.1 is now known and corresponds to [1650 AD–1683 AD]. The history of the *kinnari vina* E.1444 is now known: it was made during the [1666 AD–1690 AD] interval and its upper nut was changed before its arrival in France, likely during [1678 AD–1766 AD]. Furthermore, we have highlighted the use of bitumen-derived glue used to assemble and make the instrument.

To sum up, in this first combined museological-geochronological study performed on legacy musical instruments, we have shown that like analysis performed on archeological musical instruments, ^{14}C dating can be a powerful tool to inform not only on the creation of a musical instrument but also on its use.

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RESEARCH ARTICLE

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The story of the “Qiulai” *qin* unraveled by radiocarbon dating, Chinese inscriptions and material characterization

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Abstract

An ancient table zither *qin*, an emblematic stringed instrument of traditional Chinese music, has been rediscovered in the museum collection of the Conservatoire National des Arts et Métiers (inv.4224, CNAM collection), Paris. This instrument named “Qiulai” *qin*, whose origin is poorly documented, can claim to be one of the oldest *qin* preserved in European collections; its state of conservation is exceptional. A thorough examination was carried out based on an innovative approach combining museum expertise, material characterization analyses (optical microscopy, VIS/IR/UV imaging, X-ray fluorescence, SEM–EDS, Raman) and advanced radiocarbon dating technology (MICADAS). Our results highlight the great coherence with the traditional manufacturing practices mentioned in early Qing dynasty *qin* treatises and poems, in particular the collection of materials with highly symbolic meanings referring to the *qin* sound, nature and the universe. The reuse of resinous wood of the *Taxus* family from a building such as a temple has been demonstrated. The ash layer contains bone black, crushed malachite and residues of silica, ochres, potassium and magnesium aluminosilicates. Our study confirms the antiquity of the “Qiulai” *qin* in Europe by indicating that it was most likely made in the small [1659–1699] interval of about 30 years at the turn of the eighteenth century.

Keywords: *qin*, Chinese zither, *Tang Kai*, Musical instrument, eighteenth century, Radiocarbon dating, Spectroscopy, Qin dynasty texts

Introduction and research aims

The *qin* or *guqin* (“old *qin*”) is a seven-stringed Chinese table zither regarded as one of the oldest chordophones in China. Based on surviving early written sources and archeological findings, the instrument is attested since the Zhou dynasty (eleventh-fifth century B.C.) and its definitive organological features were established during the Western Jin dynasty (265–316) [1]. Its construction appears simple but allows a wide variety of sounds, from deep bass to crystal-clear high-pitched notes, and

finger strokes that can be or gentle or violent. This highly esteemed and mainly solo instrument connotes the refinement and sophistication of the literati, the Chinese scholarly elite, along with the practice of poetry, painting, calligraphy and chess [2]. The *qin* is considered as one of the objects that best epitomizes Chinese thought [1].

Beyond the elaborate sound images it produces, the *qin* is also revered as a refined artwork, whose shape is imbued with a strong symbolic meaning. The different parts of the instrument refer to the dragon, the phoenix, the sky and the earth. The making of a *qin* corresponds to an ideal such as a concentration of the harmony of nature, the energetic flow (*qi*), and all the forces of the Universe [1]. The materials selected are therefore invested with deep meaning, such as timber from temples that is impregnated with chanting, or from trees growing near

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water cascades, or in calm and secluded places, etc. Great value is attributed to the numerous cracks (*duanwen*) on the surface lacquer layer which are considered as a sign of "antiquity", one of the virtues embodied by the *qin* [3, 4].

The ten-year Cultural Revolution (1966–1976) in China had important consequences on the arts, including on the teaching and practice of *qin* and listening to this instrument [5]. Like other symbols strongly associated with the elites of the Old Empire, efforts were made to "target for destruction" multi-century *qin* [6]. Nowadays, modern *qin* makers, recognized as the heirs of this ancestral tradition, perform their work with the remaining knowledge that survived the cultural compliance policy under Mao Zedong [7]. Considering its long history, its numerous cultural and symbolic associations and its crucial role in the shaping of Chinese culture, the *qin*—along with its musical repertoire—was included in 2008 in the UNESCO list of Intangible Cultural Heritage of Humanity.

To our knowledge, the *qin* rediscovered in 2012 in the collections of the Conservatoire National des Arts et Métiers (CNAM, Paris) is the oldest *qin* known in European museum collections.¹ In view of the evidence in favour of its authenticity, its value is considerable. Research combining a series of scientific techniques and early written sources remains relatively inaccessible and can only be found in Chinese scientific literature or well-informed Chinese expert circles [8]. Likewise, while the literature on Chinese lacquers is abundant [9–12], few scientific reports are available on the material characterization of early *qin* lacquers [8, 13]. However, information related to the making of *qin* appears in the numerous poems praising the instrument and in ancient treatises that shed light on the origin and use of materials [14].

This article combines visual examination of the instrument by *qin* experts, material characterization analyses and advanced radiocarbon dating technology in an interdisciplinary framework. We will demonstrate that the scientific investigations on the different parts of the *qin* from the CNAM collection are consistent with the practices of *qin* craftsmanship that follow a steady tradition throughout the Qin dynasty, as depicted in the following seventeenth and eighteenth-century written sources: the *Qinfang* "Twenty Four Flavours of *qin*" which is an early treatise written c.1641 by Xu Shangying [4] and the *Yuguzhai Qinpu* "Abiding with Antiquity" written c.1860 by Zhu Fengjie which is a very popular late Qing dynasty *quqin* handbook [3].

Description of the "Qiluai" *qin*

An exceptional Chinese zither in European collections

The *qin* under study is a Chinese table zither owned by the Conservatoire National des Arts et Métiers (CNAM, inv. n° 04,224) and currently on loan to the Musée de la musique since 2015 (inv. n° D.04224) (Fig. 1). This *qin*

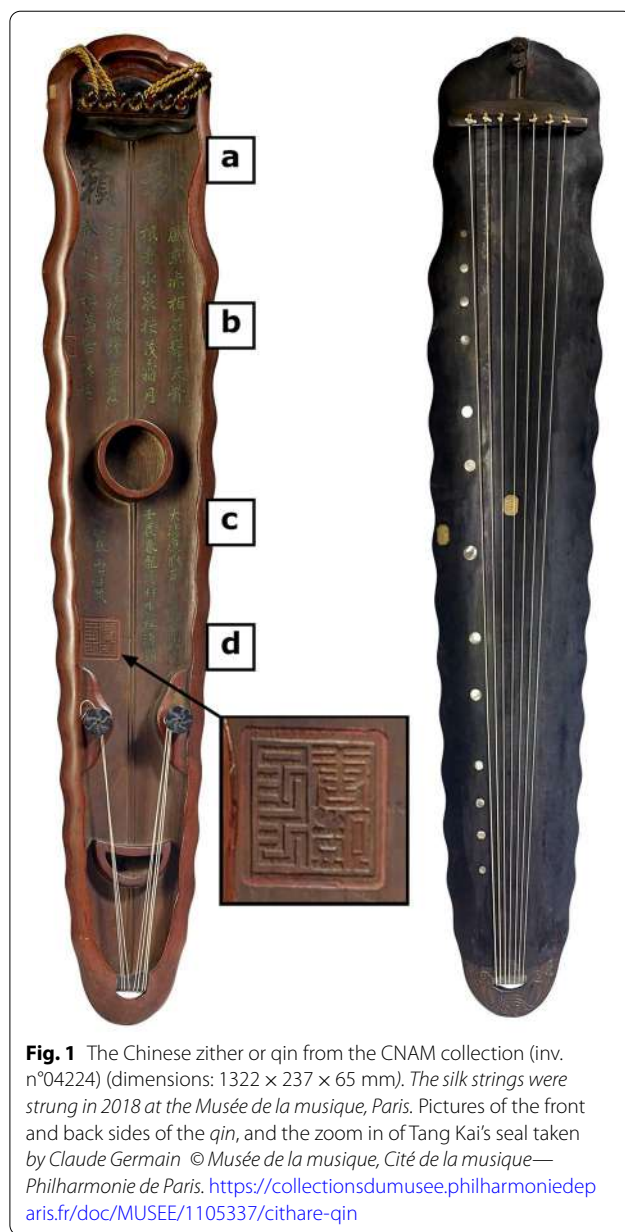


Fig. 1 The Chinese zither or *qin* from the CNAM collection (inv. n°04224) (dimensions: 1322 × 237 × 65 mm). The silk strings were strung in 2018 at the Musée de la musique, Paris. Pictures of the front and back sides of the *qin*, and the zoom in of Tang Kai's seal taken by Claude Germain © Musée de la musique, Cité de la musique—Philharmonie de Paris. <https://collectionsdumusee.philharmoniedeparis.fr/doc/MUSEE/1105337/cithare-qin>

is composed of a soundboard apparently made from a single block of wood, without a bottom, with a system of bridges, peg pool, a nut, two feet to attach seven silk strings, respectively on and under the forehead, the end (tail) and below the soundboard of the *qin* [15]. Thirteen round studs or emblems (*hui*) of mother-of-pearl are aligned to mark harmonic positions. The upper and lower parts of the *qin* symbolize the sky and the earth; two pillars under the soundboard in a circular and a crescent moon shape are called respectively the pillars of "Heaven" and "Earth" (Fig. 1). Visually, the front side is black and the back side is reddish.

¹ The MET, New York, keeps a *qin* that belonged to Prince Lu and dated from 1644. <https://www.metmuseum.org/art/collection/search/503523>.

This *qin* was rediscovered in 2012 during the “récolement”² of the musical instruments of the CNAM acoustic collection. Philippe Bruguère, the former Curator of non-European collections at the Musée de la Musique, suspected its old age. The Musical Instrument Museums Online database (MIMO)³ was queried to compare this instrument with other *qin* listed in partner museums, as well as for *qin* from private collections [16]. The *qin* has exceptionally rare features with a leaf banana shape known as *jiaoye* 蕉葉 style and the absence of a bottom. The shape and the carved date situate its manufacturing period during the 17th or eighteenth century in China. For comparison, the “Gumeihua” *qin* with a similar shape in China (Forbidden City) was made during the Ming 明 dynasty (1368–1644) and once belonged to the collection of the Emperor Qianlong 乾隆 (1735–1796) [17]. The rediscovered *qin* is assumed to be one of the oldest *qin* kept in European museum collections.

Despite previous studies based on the CNAM archives and inventories, its provenance remains mysterious. The CNAM was created in 1794 following decrees issued during the French Revolution to promote national industry. The researchers of the CNAM gathered the following clues [18]:

- The presence of musical instruments is attested since 1814 at the CNAM with the installation of the early “Cabinet de physique de M. Charles” who was elected as a physicist to the Académie des Sciences in 1785 [19].
- The *qin* n°4224 is clearly mentioned in the inventories edited in 1849 at the Conservatoire⁴ for the creation of the acoustics gallery in 1851–1852.
- Objects with inventory numbers around 4000 were presumably kept at the Académie des Sciences prior to their transfer to the Conservatoire.⁵ The Académie des Sciences was initially created in 1666 as an informal scholarly circle and kept collections of objects for scientific studies and education. Some objects were taken from these collections to complete the collection of the Conservatoire after the French Revolution.

² An operation to check the presence of documents and objects in the collections of French national museums updated every ten years.

³ MIMO: Musical Instrument Museums Online—<http://www.mimo-international.com/MIMO/> (accessed: 21/05/03).

⁴ A figure of the *qin* is also briefly presented in the official catalog of the Conservatoire collections from 1905: “King” (Fig. 12 no. 4224) Chinese stringed instrument”. The term “Conservatoire” is used here to avoid anachronisms due to the numerous changes of name of the CNAM over time.

⁵ The objects with inventory numbers from 3570 to 4541 do not have a well-documented provenance. They likely came from the Académie des sciences in Paris, but they may also have come from property seized by revolutionaries from nobles who fled France during the French Revolution, or from lootings during Napoleon’s conquests across Europe.

Inscriptions and meaning

The inscriptions engraved on the back side of the *qin* are reported in Fig. 2. First, they refer to the name of the instrument “Qiulai” 秋籟 meaning “Autumnal resonances” (Fig. 2a). The following inscriptions in carved Manchu reproduce an extract from the famous poem “Qinzan” 琴贊 “In praise of the *qin*” written by Li Bai 李白 (701–762) (except the first verse and some slight modifications in red (Fig. 2b)). The bottom part of the inscriptions includes information on the making of the instrument (Fig. 2c) and Tang Kai’s seal (Fig. 2d). Tang Kai 唐凱 was a well-known court zither player and zither maker, as well as a *qin* collector during the reigns of the Chinese emperors Yonzheng 雍正 (1722–1735) and Qianlong 乾隆 (1735–1796) of the Qing 清 Dynasty (1636–1912) [17]. The inscription Songtao 松濤 “gusts of wind in the pines” refers to the nickname of Tang Kai whose complete *hao* (i.e. pseudonym) is Longwan *cunso* 龍灣村叟松濤 “the so-called old man of the gusting wind in the pines of Longwan”.⁶ According to the carved inscriptions (Fig. 2c), the making of the *qin* is dated 1712, which is consistent with the period of activity of Tang Kai. This maker is known to have owned seven ancient *qin* 古琴 with similar inscriptions and the same seal as the “Qiulai” *qin* [20]. However, no early written sources mentioned this “Qiulai” 秋籟 *qin* in his collection, even though the name is common for a musical instrument.

Material composition

Wood

The monoxyloous wooden body of the “Qiulai” *qin* is made of the light porous brown resinous species from the *Taxus* genus belonging to the *Taxaceae* family.⁷ The forehead of the *qin* has been carved in hardwood teak, i.e. *Tectona grandis* from the *Lamiaceae* family.

Based on the legacy of the surviving written sources and the practices of modern makers, the commonly mentioned wood species for each part of the instrument are as follows [14]⁸:

- For the soundboard: *tong* 桐 tree, *wutong* 梧桐, *paotong* 泡桐, *qingtong* 青桐, etc.; or spruce 雲杉, or cedar *shan* 杉 or “cloud fir wood” *yunshan* 雲杉.

⁶ Personal communication from François Picard (2013/12/17).

⁷ Botanical identifications performed by Victoria Asensi (©Xylodata), 2015/01/14, and by Catherine Gill (Laboratoire de Paléobotanique, Université Pierre et Marie Curie, Paris), 2015/04/14, based on micrographs taken by Anne Houssay with an optical microscope Zeiss Axio Scope.A1 Vario and by comparing to a database of Chinese forests (<http://www2.ffpri.affrc.go.jp/fdb/esawoodq/wood.html>). Reports available at the Musée de la musique.

⁸ Wood species listed in a personal communication from Lucie Rault (2021/03/29).


Original inscriptions	Translations
<p>a 秋籟。</p>	<p>Autumnal resonances¹</p>
<p>b 峰阳孤桐，石耸天骨。 盛京赤柏</p> <p>根老冰泉，叶苦霜月。 枝茂</p> <p>斫为绿绮，徽声粲发。 徽音</p> <p>秋风入松，万古奇绝。 清</p>	<p>Upon the craggy slopes near the peak, <u>the solitary tong tree</u>² crimson cypress of Shengjing</p> <p>Hoists itself upon the rock like some celestial skeleton</p> <p>Its venerable roots appear as streams stilled by frost</p> <p>And <u>its fragile leaves</u> as though iced by the moon its lush branches</p> <p>Its wood is carved to produce the most exquisite instrument, Whence <u>the notes</u> exuding from its emblems³ sparkle as they spread, delicate sounds</p> <p>Resonating like the autumn wind that passes through the pines: <u>A wonder</u> that will remain forever unequalled! crystal-clear</p>
<p>c 大清康熙五十一年歲次， 王辰春龍灣村叟松濤斫</p> <p>橫琴山廬藏</p>	<p>51st year of the Kangxi era of the great Qing⁴</p> <p>The old man Songtao carved the instrument in the village of Longwan in spring 1712⁵</p> <p>Hoarded in the hermitage of Hengqinshan («horizontal qin mountain»)</p>
<p>d </p>	<p>Tang Kai's seal</p>

Fig. 2 The inscriptions carved on the back side of the qin and their meaning: **a** the name of the qin: ¹lai籟 is a polycalamus flute of the yue 龠 type with three holes. The qin tends to reproduce the soft and nostalgic sounds of this "antique" flute suggesting an autumnal atmosphere. **b** "In praise of the qin", Li Bai's poem (translation by Lucie Rault): the original text is in black, the modified passages carved in the qin are in red and under the corresponding sonograms. ² tong 桐 (in original version) or wutong 梧桐 [21]. ³ hui 徽 studs that mark harmonic positions, **c** information on the making of the qin: ⁴ dated from 1712 according to the era mentioned under the Qing Dynasty, ⁵ dated from the spring of the year renchen 壬辰, which is the name of the sexagesimal year corresponding to 1712 (according to the cyclic calendar), **d** Tang Kai's seal

- ii. For the back side: *zi* 梓 or *qiu* 楸 trees, i.e. catalpa; or *qi* 漆 tree i.e. *Toxicodendron vernicifluum* or lacquer tree.
- iii. For the foot: *wu* 烏 tree, i.e. black ebony.

The *Taxus* wood is not a conventional wood used in the making of qin since the Chinese literature and tradition mainly cite the *tong* 桐 tree as the foremost wood used [3, 14, 22].

Coating

The wooden body of the "Qiulai" qin is completely covered with black and red coatings, providing a strong impression of the homogeneity and cohesion sought by the qin maker [4]. We will choose the term "lacquer" in the following due to the traditional use of raw tree lacquer as organic binder (Additional file 1: Fig. S1). Traditionally, the lacquer ash layer *huitai* 灰胎 is applied on the wood support as the preparation layer. It is usually

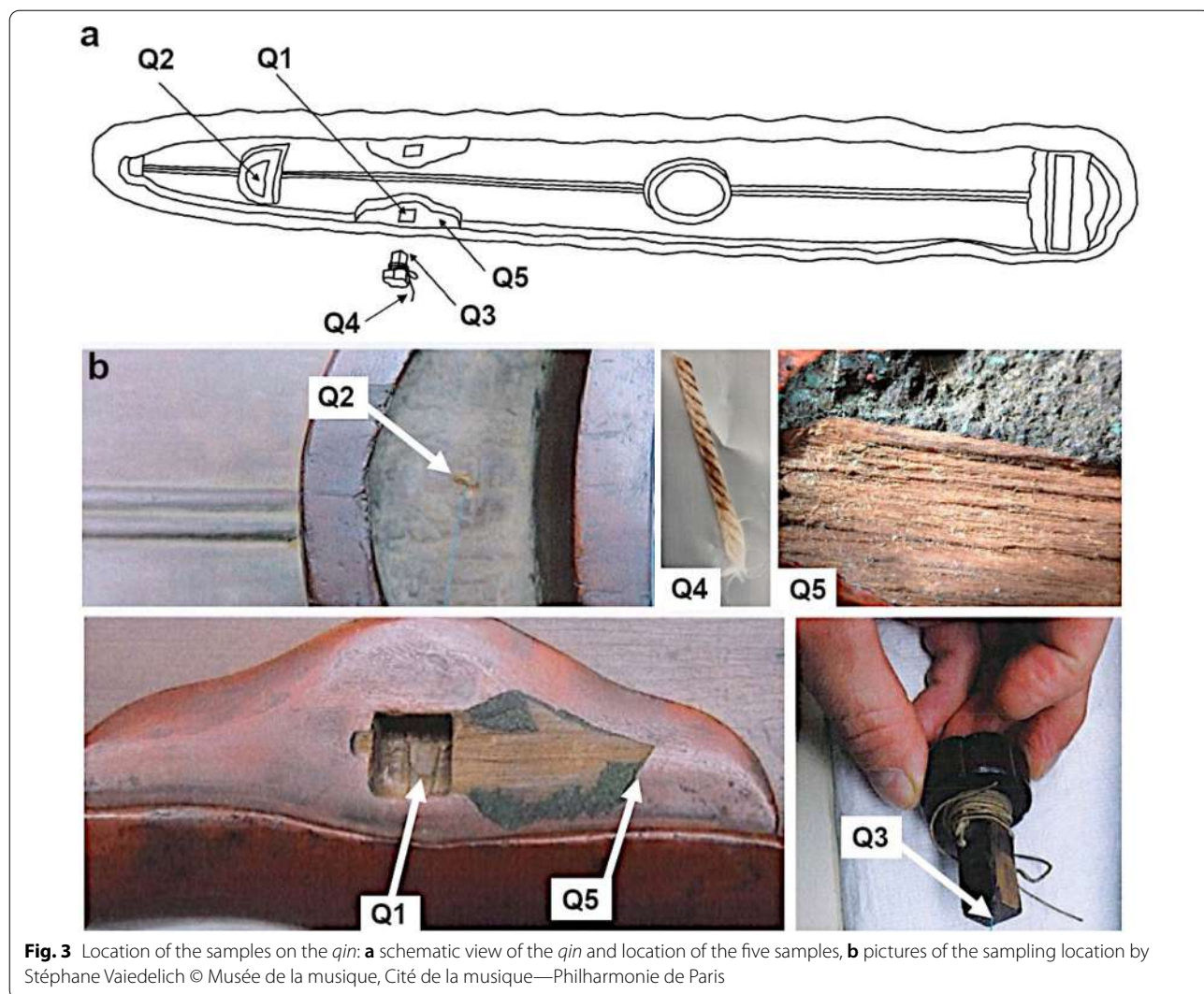


Fig. 3 Location of the samples on the *qin*: **a** schematic view of the *qin* and location of the five samples, **b** pictures of the sampling location by Stéphane Vaiedelich © Musée de la musique, Cité de la musique—Philharmonie de Paris

described as a miscellaneous mixture of *Toxicodendron vernicifluum* lacquer, deer bone powder, deer antler, pig's blood, brick, lime, mother-of-pearl, gypsum, gold, silver, jade, agate, coral, shells, etc. The lacquer was applied in several layers to give the finishing veneer. Great value is attributed to ancient *qin* whose lacquer layer is marked by numerous cracks named *duanwen* 斷紋. Surprisingly, the lacquered surface of the "Qiulai" *qin* has no cracks (*duanwen*).

Silk

The strings that were found knotted around the feet and the bridge prior to their changes in 2018 are made of silk (Fig. 3). The silk came traditionally from insect cocoons

named *jiacan* or domestic silkworm in Chinese and the species used is *Bombyx mori*. A coating of dirt, glue or wax on the surface of the strings is visible, ranging from off-white to brown-black. Early recipes suggest the use of fish glue, wax or boiled rice for the impregnation of boiled silk strings that helps hold the fibers together and influences the sound [3].

Methods

Sampling

Micro-sampling was performed on the *qin* for radio-carbon dating. The size of the samples ranged from 0.2 to 1.4 mg on discrete parts of the back of the body of the *qin* in order to respect the aesthetic integrity of the object (Fig. 3, Table 1).

Table 1. Description of samples Q1 to Q5.

Sample	Location	Material composition
Q1	Bottom of the foot pool	Wood
Q2	Pillar – back of the qin	Wood
Q3	Foot	Wood
Q4	String	Silk
Q5	Coating crack near the foot pool	Coating stratigraphy

Material characterization analyses

Optical and digital microscopy

First, the stratigraphy of the lacquers was observed in-situ under visible (VIS), infrared (IR) and ultraviolet (UV) rays using VIS/IR/UV imaging on a Dino-Lite with DinoCapture 2.0 software. Then, a chip of the coating, which comprises the complete stratigraphy from the surface to the wood support, was investigated using light microscopy (Zeiss Axio Scope.A1 Vario) and digital microscopy (3D Keyence-VHX).

X-ray fluorescence

A preliminary investigation was done using X-ray fluorescence spectrometry (XRF) Jetstream M6 from Bruker with a rhodium anode in the X-ray tube at 50 kV and 200 μ A with a 100 μ m-thick beryllium window. The beam diameter was 450 μ m. The target was placed horizontally at a working distance of 2 mm. The spectra recording time was 200 s, with a maximum count rate of 96 kcps. Data were processed with the Esprit software developed by Bruker [23].

MEB-EDS

The coating sample was embedded in a polyester resin ESCIL-SODY 33, pre-polished with SiC papers, to obtain a transversal section. Analyses were then performed using Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM–EDS) with the JEOL-JSM IT 300 instrument (mode 'HighVacuum', WD = 10 mm, an energy beam of 20 keV, mode BED-C) and an X-ray microanalyzer X-MaxN (Oxford). The results were processed with Aztec software (Oxford).

Raman

Two different Raman instruments were used. The microspectroscope Raman confocal INVIA Renishaw with a laser source of 532 nm was used for the black layer of the transversal section of the coating (see “General description of the lacquer layers”). The microspectroscope Raman with a laser source of 785 nm from BWTek was

Table 2 Description of the sub-samples Q5-1 to Q5-3

Sub-sample	Location	Description of the layers
Q5-1	Coating crack near the foot pool	Wood under the black lacquer
Q5-2	Coating crack near the foot pool	Black lacquer
Q5-3	Coating around the foot pool	Reddish lacquer

used for the red layer of the transversal section of the coating (see “General description of the lacquer layers”). The systems were equipped with an optical microscope (confocal mode, focus \times 50).

¹⁴C analyses

Sub-sampling of the coating

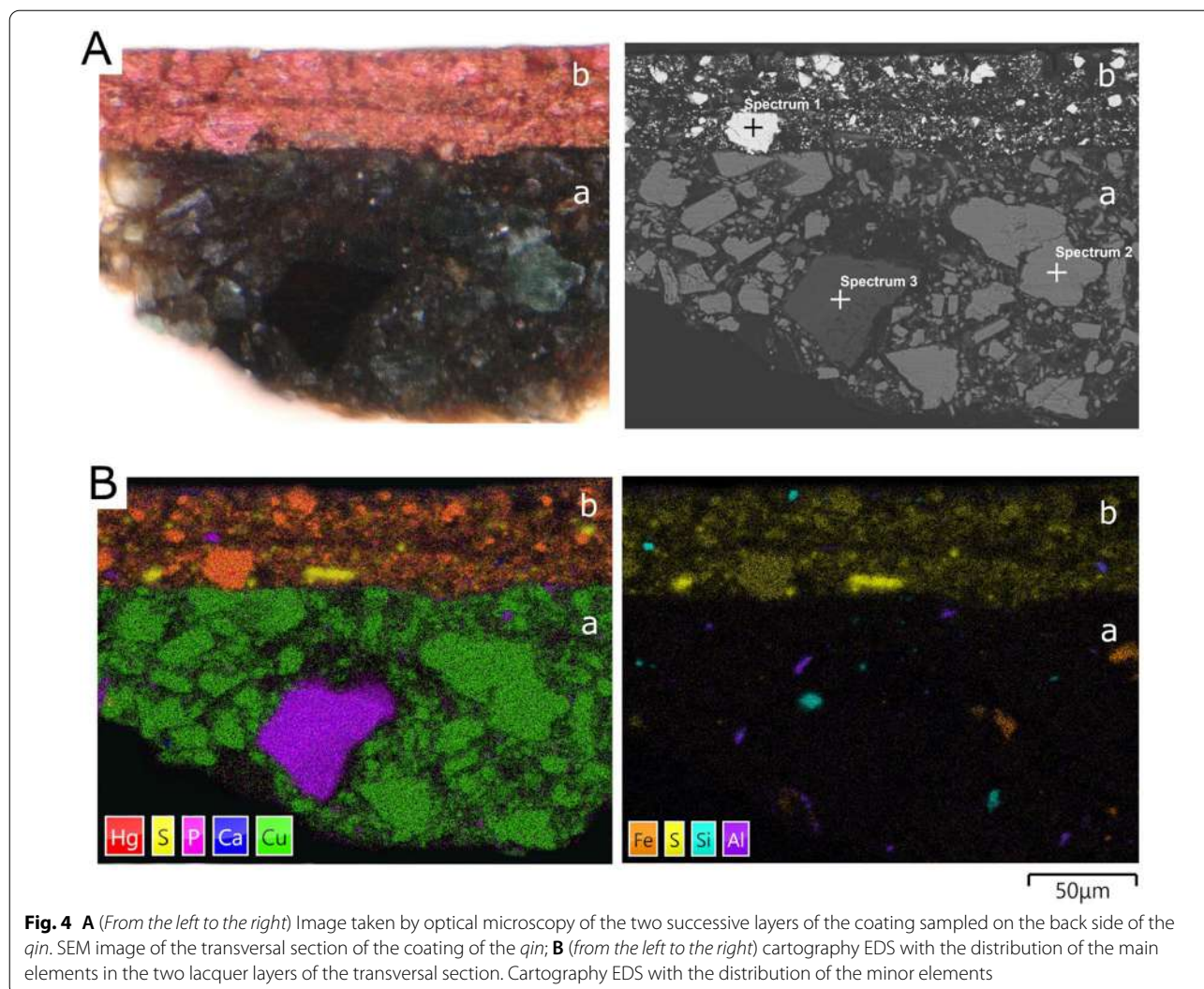
Q1, Q2, Q3 and Q4, were sampled using a cleaned chisel (Fig. 3). The multi-layer lacquer sample Q5 (see “General description of the lacquer layers”) required a more elaborate mechanical treatment using microchisels (0.125 mm, 0.25 mm and 0.5 mm) in order to produce separate ¹⁴C measurements on: (1) the wooden support, (2) the black preparation layer and (3) the reddish finishing lacquer (Table 2). Solvents, commonly used by restorers to separate layers, were excluded because they induce carbon contamination. The black lacquer sub-sample Q5-2 was isolated from the wooden sub-sample Q5-1 using a microchisel on sample Q5 under binocular microscope (Table 2). The reddish lacquer layer sub-sample Q5-3 was collected in-situ using microchisels under binocular microscope after removal of a light brown film of dust by scraping with a microchisel (Table 2).

3.3.2. Chemical pretreatment for ¹⁴C dating

The wooden and silk samples were treated with the classical AAA chemical protocol suitable for wood and charcoal [24] as follows: (i) HCl 0.5 M (room temperature) and rinsing with ultrapure water until pH = 5, (ii) NaOH 0.1 M (room temperature) and hot rinsing (80 °C) until pH = 5, and (iii) HCl 0.5 M (room temperature) rinsing until pH = 5. As dust was expected to be the potential lacquer contamination, Q5-2 and Q5-3 underwent acid treatment with HCl 0.5 M, at ambient temperature and rinsing until pH = 5.

Chemical glasses and protective aluminium foils were previously baked out at 450 °C during 6 h, making them carbon-free. All chemicals were of ultrapure quality, and water was ultrapure (MilliQ grade).

To control the impact of chemical treatment and of the combustion, we also ran in-house “blank” (AfSud, a 70 kyr charcoal from Border Cave, South Africa) and



international standards (wood—SIRI G at 378 ± 39 BP [25]).

CO₂ conversion and physical measurement

The mass spectrometer *ECHoMICADAS* was used to measure the ¹⁴C activity of each sample [26, 27]. All the samples (from 40 to 160 µgC) were directly injected into an elemental analyser (EA) coupled with the MICADAS gas source through the gas ion source interface (GIS) [28]. The red lacquer sample Q5-3 was an exception and was injected as a gas into the MICADAS gas source through the GIS by tube cracking [29]. CO₂ was obtained off-line by combustion under pure O₂.

Ages were obtained from ¹⁴C measurements using *Bats* software by comparing ¹⁴C/¹²C ratios with OXII standards [30]. Most of the samples provided several measurements, but results were statistically combined.

The mean age of the sample then derives from the mean of the individual measurements, which pass the Chi² test, and is associated to the maximum between the Chi² reduced error and the standard deviation between the median of the individual measurements. Results are expressed in F¹⁴C as recommended by Reimer et al. [31] and provided as ¹⁴C ages (BP) following Stuiver and Polach's convention [32]. Probability distributions of calibrated ¹⁴C ages were generated using OxCal v4.3.2 [33] based on the IntCal20 calibration curve [34].

Results

Material characterization

General description of the lacquer layers

The optical microscopy revealed that the lacquer on the back side of the *qin* comprises two successive layers: (a) a heterogeneous black layer of around 1 mm with greenish

grains applied on the wooden support, (b) a homogeneous reddish surface layer of 35 μm lightly covered with a dust deposit (Fig. 4A). According to measurements using XRF, the two layers comprise mainly iron and copper inorganic elements.

The black lacquer

This layer is black under visible (VIS) and infrared (IR) rays using VIS/IR/UV imaging. Hence, it contains a black pigment absorbing VIS and IR rays, which cannot be iron oxide since it reflects IR rays. We deduced that the pigment is most likely a carbon black: soot, charcoal, stone black, ivory black, vine black or bone black. Respectively using SEM-EDS and Raman spectroscopy, the matrix was identified as being mainly constituted of a filler made of bone black ($\text{Ca}_3(\text{PO}_4)_2$) with coarse-grained malachite ($\text{CuCO}_3(\text{OH})_2$) (Fig. 4B). SEM-EDS analyses also detected silica SiO_2 , ochres (FeOOH , Fe_2O_3) with potassium and magnesium aluminosilicates (Fig. 4B).

The red finishing lacquer

This layer is red under visible (VIS) and slightly reflective under infrared (IR) rays using VIS/IR/UV imaging. Since XRF analyses applied on the sample Q5 mainly detected Cu and Fe, we first surmised that the red pigment could be an iron oxide. However, using SEM-EDS and Raman spectroscopy (Figs. 4, 5, 6), the red layer was identified as being mainly constituted of a mercury sulfide (HgS) most likely from the mineral named cinnabar accompanied by sparse particles of pure sulphur (S) (Fig. 4B).

^{14}C dating results

The sample Q5-2 on the ash lacquer was thick enough to perform four measurements using radiocarbon dating (Additional file 1: Table S1, Fig. 7a). The heterogeneity of these measurements with a weak A_{comb} of 5.4% is consistent with the composition of the lacquer ash layer as a mixture of several solids. The ^{14}C dating mean value obtained [69AD–245AD] is incompatible with the historical information gathered on the "Qiulai" *qin*.

The wooden samples Q1, Q2, Q3 and Q5-1 yielded similar ^{14}C results. The combination of the results using the "combine" option of Bayesian modelling [33] gave a high agreement index $A_{\text{comb}}=114.1\%$. It can be concluded that the wood pieces chosen for the manufacturing of the *qin* are contemporary. The tree or trees used grew and were cut during the [1458AD–1528AD] or [1552AD–1634AD] intervals (Additional file 1: Table S1, Fig. 7b).

The silk string sample Q4 and the red lacquer sample Q5-3 present similar ^{14}C results (Additional file 1: Table S1). The combination of these measurements,

acknowledged by a high A_{comb} value of 110.9%, highlighted that the silk strings and the red lacquer are contemporaneous, which might provide the last period of lacquering and changing of the strings on the *qin*. Considering that the presence of the *qin* in the CNAM collections is attested since 1849 (*terminus ante quem* in the Bayesian analysis), this probable last maintenance in playable condition might be included in the following intervals: [1659AD–1699AD] (25.0%), [1721AD–1814AD] (66.6%) or [1834AD–1848AD] (3.8%) (Fig. 7c).

Discussion

Characterization of the wooden body

The radiocarbon results are consistent with a traditional practice of reusing a symbolic wood when making a *qin*, as explained in "Abiding with Antiquity", c.1860 [3]. The radiocarbon dating results provide a significant hiatus, that could reach several centuries, between the dating of the wood in the [1458–1528] or [1552–1634] intervals and the dating of the silk string and red finishing lacquer (Fig. 7). The hiatus is relevant to the Chinese tradition which symbolically associates the material quality of "a very old *tong* wood" with the quality of the sound. This virtue of "antiquity" is cited in the "Twenty-Four Flavours of *qin*", ca. 1641, and detailed in the introduction by Goormaghtigh, as part of the aesthetic canons [4]. Such a music appreciation is still controversially present in the modern practice of carving *qin* in a wood that has been stored for more than a hundred years [36]. However, the storage of wood through several generations of *qin* makers is not attested in the past.

The dating hiatus between the wood on the one hand and the red lacquer and string on the other cannot be due to the sun-drying of a multi-century old tree trunk. The wood used to make the *qin* should be porous, light, even and smooth without the knots or distended and twisted fibers caused by the influence of the sun or the wind on the growth of the wood, as mentioned in early written sources. Therefore, secondary branches are preferentially selected according to an appropriate age and height [22]. The Tang period poems (618–690, 705–907) studied by You [14] confirm the preference for secondary branches rather than the trunk, except in the case of a tree less than a decade old.

"As for the material that should be used, it should be from younger branches; that is, branches that are close to the top of the trunk. If the tong is not old, then its young branches will certainly not be big. Choose wood far away from the ground, with the top blown by wind and dried by sun. It should

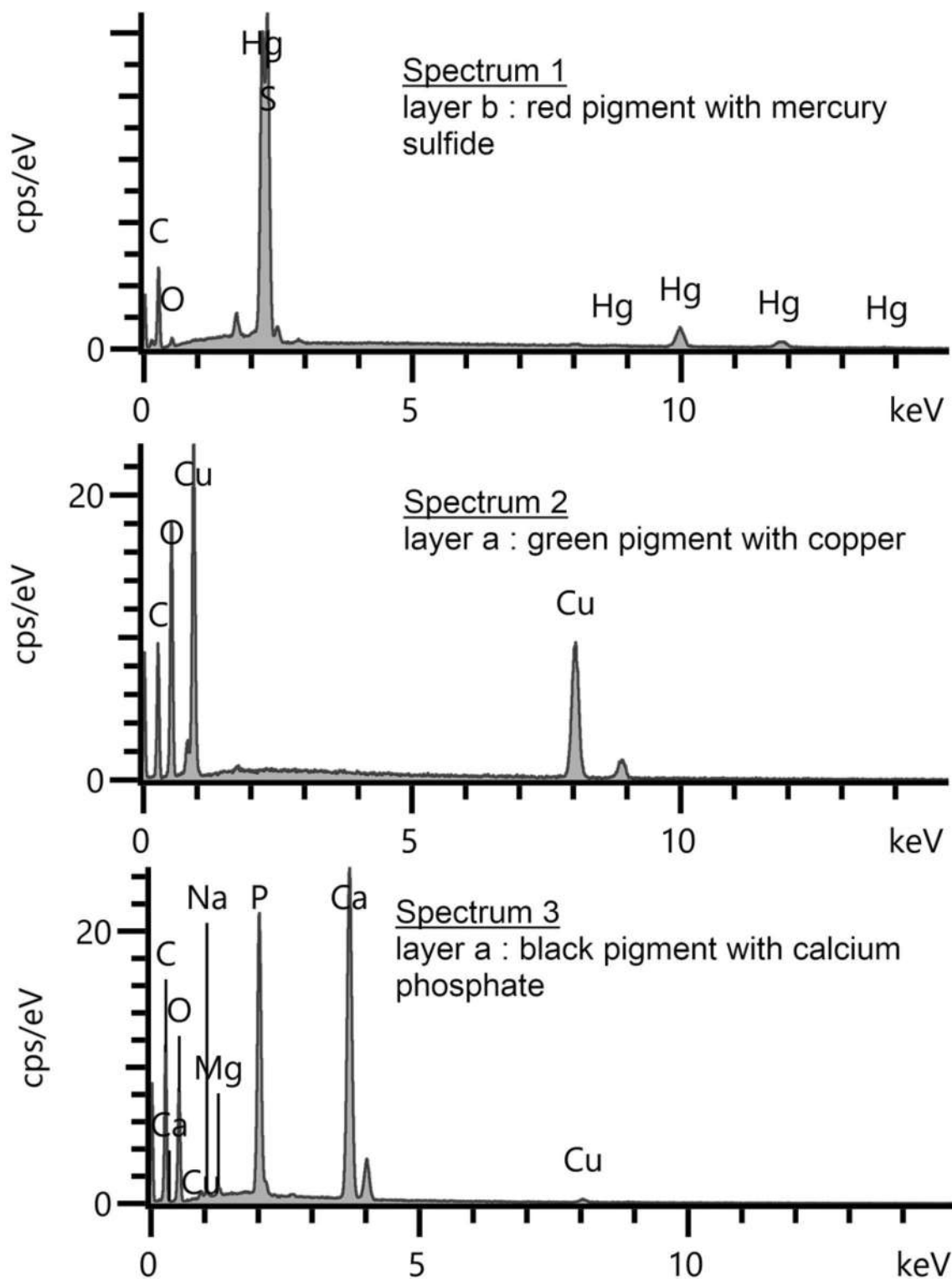


Fig. 5 The upper spectrum correspond to the homogeneous red lacquer (b), and the following spectra to the heterogeneous black layer (a) and were obtained using SEM-EDS

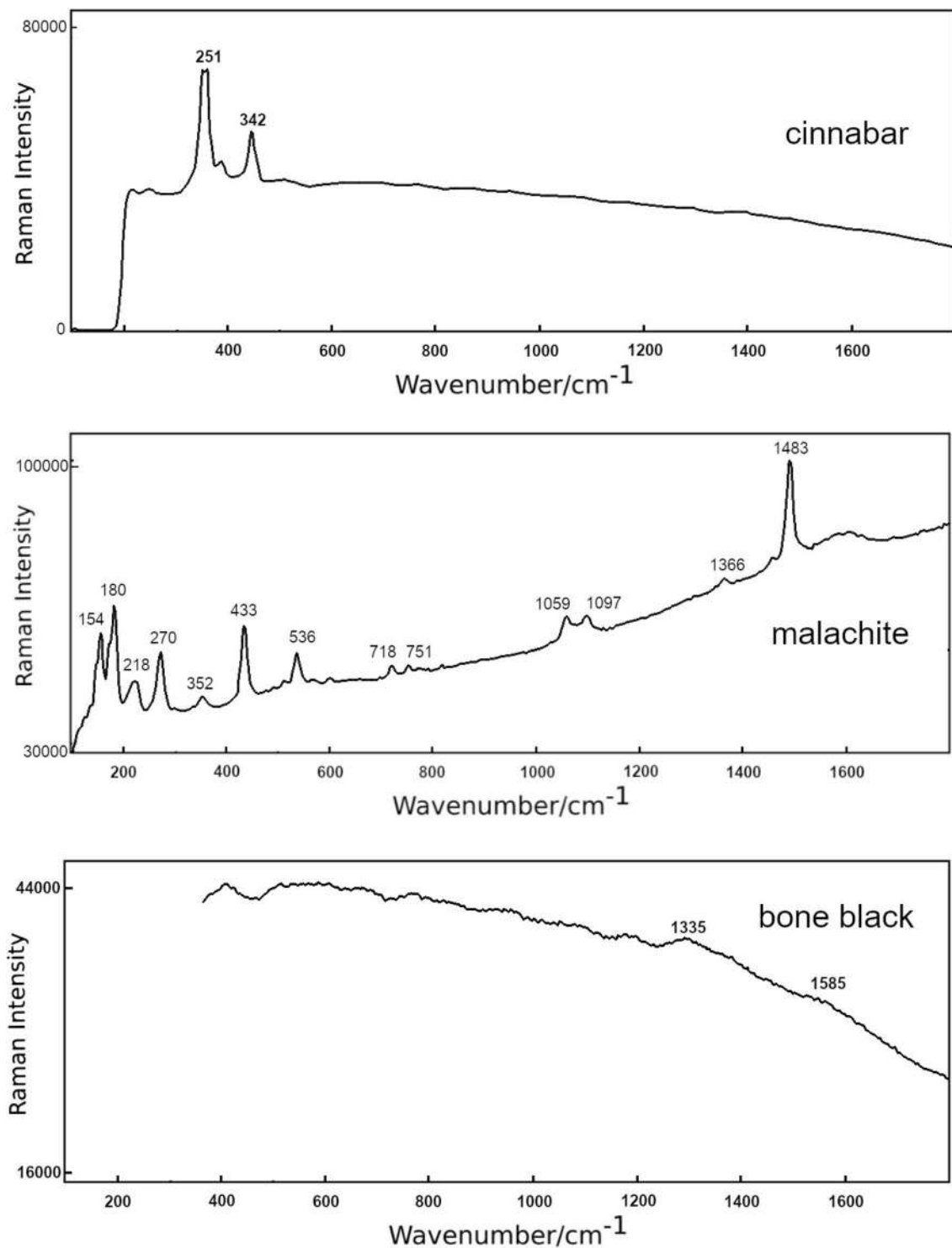


Fig. 6 (From the top to the bottom) Raman spectra for the identification of mineral pigments in the finishing lacquer (b) with some red grains showing the presence of cinnabar, and in the black lacquer (a) with several coarse green grains showing the presence of malachite, and with grains of bone black [35]

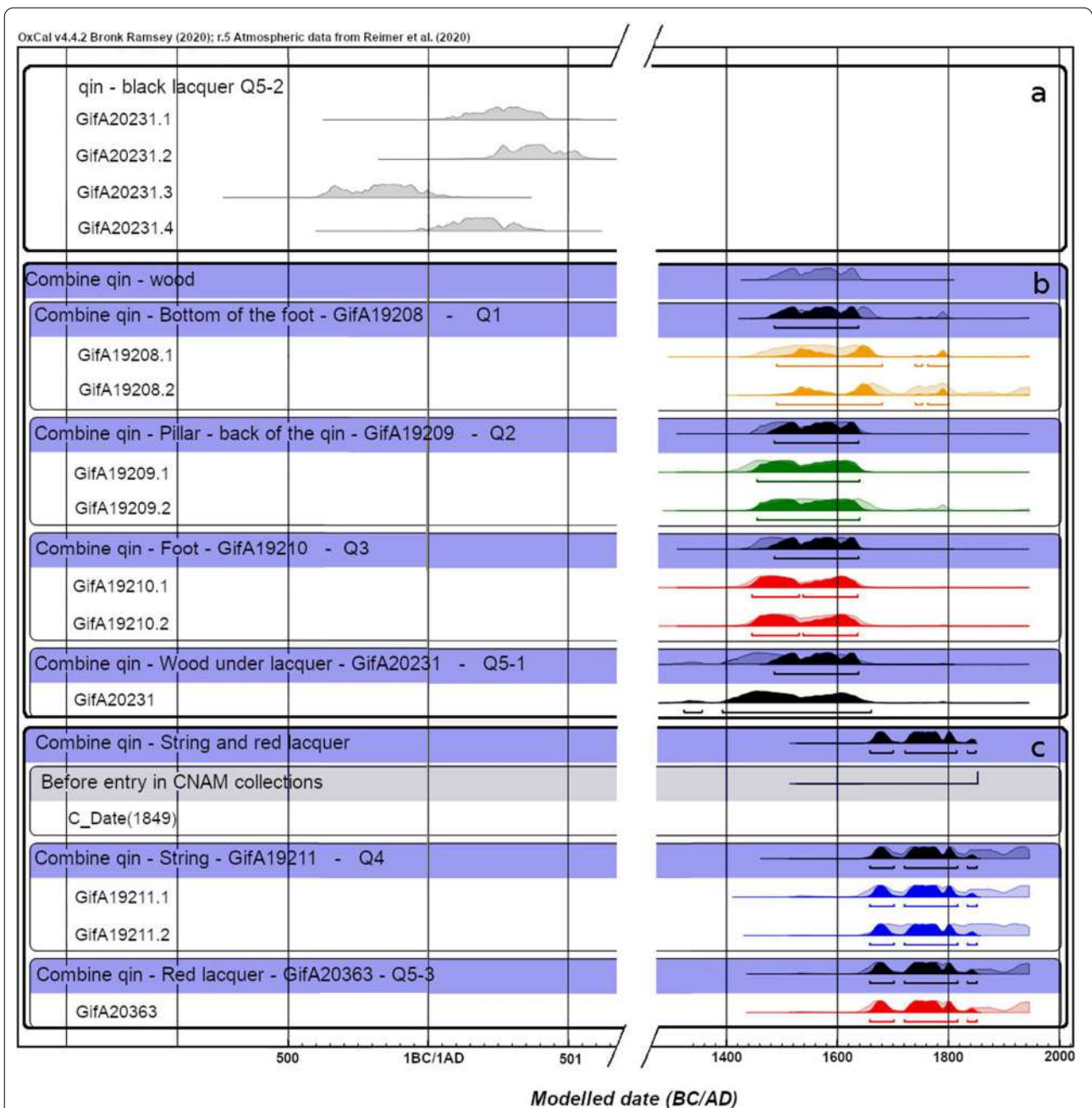


Fig. 7 Calibrated ¹⁴C ages of the "Qiu' qin. The probability distribution diagrams of: **a** sub-samples of the black lacquer Q5-2; **b** wooden samples of the back side of the foot Q1, the pillar Q2, the foot Q3 and the wood support under the lacquer Q5-1 with their respective Bayesian modeling combination in black, and the upper diagram in blue of the combination of all wooden parts; **c** sub-sample of the upper lacquer in red Q5-3 and sub-samples of the silk string in blue Q4 with their respective Bayesian modeling combination in black, and the upper diagram in black of the combination of the red lacquer and the silk string parts taking into account the event of the entry of the qin in the CNAM collection prior to 1849

be moistened by frost and dew with plenty of pure air. Furthermore, it is good if the material is facing southeast, (because) "the Great Brightness (the sun) is born in the east".⁹

The *Book of Odes*¹⁰ states: "The wutong grows there on those slopes and faces the sun"¹¹ [3]

The interpretation of the ¹⁴C results as due to the reuse of wood is reinforced by the fact that the "Qiulai" *qin* is not made from a conventional *tong* species, but from a porous resinous wood from the *Taxus* family. Considering that the changes in Li Bai's poem carved on the back side are a subtle and skilful adaptation to this particular *qin*, the replacement of the sinogram *tong* 桐 by *bai* 柏 for resinous woods of cedar or cypress may be linked to this manufacturing choice. Other wood species than *tong* tree can be used, especially old building timbers:

"As for good quality in old materials, (...) one cannot be certain that it will be *tong* wood. Some other kinds of wood are also all right. The wood is useable as long as it is light and porous, crisp and smooth. (...) As for beams, pillars, and router rafters, the ancients used *tong* for some of these. But it has to have survived for a couple of hundred years. If at an old monastery or temple on a high precipice or cliff, or by a waterfall, or stream shore in high, spacious and quiet regions, absolutely cut off from the cacophony of the everyday world, there one can find good material for the *qin*. Naturally it will have a special sound." [3]

As a testimony of this practice during the nineteenth century, the wood of the "Yun He" 雲龕 *qin* kept at the Musical Instruments Museum, Brussels (Coll. MIM, n° inv. 0760) has been identified as originating from Jing Hui 淨慧寺 Temple in the Guangzhou province (Canton) thanks to ink inscriptions on the back side [37]. This unfulfilled epigraph also indicates that the *qin* was built by the maker Li Menggeng 李夢庚 whose life is poorly known, but who partly coincides with the reign of Daoguang 道光帝 (1820–1850). The entry of this *qin* in the MIM collections is dated between 1881 and 1886 according to the inventories.

The ¹⁴C results for the wood of the "Qiulai" *qin* are consistent with a long tradition in *qin* making that consists in reusing old wood with a highly symbolic and spiritual

value, whether during the period of activity of Tang Kai or in the early nineteenth century before the recorded presence of the *qin* in the CNAM collection in 1849.

Composition of the lacquer ash layer

The radiocarbon dating and material characterization of the "Qiulai" *qin* lacquer ash layer revealed a mixture of two major solid ingredients, bone black and malachite, consistent with the use of powdered deer antler and crushed stones mentioned in the *Qinfang* c.1641 and the *Yuguzhai Qinpu* c.1860 [3, 4]. The lacquer ash layer is located between the wood body and the red lacquer. However, the heterogeneous ¹⁴C results on this layer with a mean value of [69AD–245AD] are not compatible with the expected period of the making of the *qin*. Based on the material analyses, the age obtained might be due to the mixing of carbon from ingredients contemporary with the lacquering of the *qin* ($F^{14}C = 0.976 \pm 0.007$, value of the red lacquer) with 20% of geological carbonates from malachite residues ($F^{14}C = 0$) remaining after acid etching during the chemical pretreatment of the sub-sample Q5-2.

The detection of carbon and phosphorous in the lacquer ash layer of the "Qiulai" *qin* does not differentiate deer antler ash from deer or another animal bone ash. Li et al. [13] also reported that the detection of $Ca_3(PO_4)_2$ merely indicates the presence of bone ash regarding the "Yu Quan" *qin* from the Yuan Dynasty. However, traditional recipes comprising the raw sap of the lacquer tree and the ash of deer antlers *lujiao shuang* 鹿角霜 are mostly cited [14, 38]. According to the *Yuguzhai Qinpu* c.1860, "Whenever others put on the powder and lacquer they use a cattle horn comb (...). The powder; that is, deer horn *shuang*霜, (...) should be ground fine."

The detection of the coarse grains of malachite is suggestive of the *qin* makers' practice of occasionally adding fragments of metal or stone to the lacquer ash layer in accordance with the symbolism of the carillon and lithophone so as to obtain the ideal acoustic properties, as discussed by Goormaghtigh [4] based on the following citation in the *Qinfang* c.1641: "The fingers struck the strings as if they drummed metal or stone, without any interference from the neighboring strings. It is in this search for limpidity that one goes beyond all sounds". Chang [39] mentioned that the highly estimated lacquer of *qin* made in the Tang Dynasty (618–690, 705–907) corresponded to the Asian lacquer technology consisting in adding scraps of metallic or stone fillers. A mixture, commonly named "eight precious ash" lacquer *baobaohui* 八寶灰漆¹² by *qin* makers, is made of fragments of gold, copper, bronze, porcelain, silver, mother-of-pearl, malachite, pearl, jade, agate, coral or seashells [8].

⁹ *Da ming sheng yu dong* 大明生於東 *Liji* 禮記 (Book of Rites), *Liqi* 禮器 (Instruments of rites, 28, <https://ctext.org/liji/li-qi/zh>).

¹⁰ "wutong sheng yi, yu bi chaoyang 梧桐生矣, 於彼朝陽。" *Shijing* 詩經, 252 <https://kknews.cc/culture/5lly9g3.html>.

¹¹ The *Yuguzhai qinpu* http://web.cecs.pdx.edu/~jrb/chin/v22/v22.htm#_ftnref7.

¹² <http://www.silkqin.com/03qobj/strings/shuchee1.htm>.

Powdered deer antler and crushed stones are not ingredients only used for *qin* lacquers but can be found in Asian lacquers of other objects [40]. For example, a lacquered tray from the Ming period (1368–1644) presents surface "snake-belly cracks" as for *qin* from the same period, which could be due to the use of similar compounds such as powdered deer antler, bone, horn, ash, sandstone, or ceramics [41]. Our results are consistent with the traditional composition of the lacquer ash layer of *qin*; however, due to the long tradition spread over several dynasties, a more accurate attribution is not possible.

The silk string and the red lacquer dating

The analyses revealed that the remaining silk string and the red lacquer are contemporaneous, meaning that the last lacquering and maintenance in playable condition occurred in China during the Qing dynasty (1644–1912) since the radiocarbon dating yielded the [1659–1699], [1721–1814] or [1834–1848] intervals. According to our investigations, three hypotheses are currently available for the attribution of the period when the "Qiulai" *qin* that entered the CNAM collection before 1849 was built: (i) it was collected, dated and signed by Tang Kai in 1712, (ii) it was made by Tang Kai in 1712, or (iii) it is a well-informed late eighteenth-nineteenth century copy using an old wood carved in China.

The absence of typical cracks *duanwen* 斷紋 on the lacquer is surprising. Cracks may begin to appear a hundred years after the making, and the shape of the cracks can be used for the relative dating of the *qin*. Re-lacquering or restoration of the "Qiulai" *qin* by successive owners can be considered during the [1721–1814] or [1834–1848] intervals, as such practices have already been observed on other ancient *qin*.¹³ For example, the "Mingfeng" 鳴鳳 *qin* is known to have been recut and re-lacquered by Tang Kai [20]. The cracks on the "Xianren you" *qin* from the Song period (1127–1279) have been wiped out by restoration [42]. However, the cracks are not necessarily proof of antiquity even if this is the reason why Chinese connoisseurs estimate them. Like the "Qiulai" *qin*, the "Yun He" *qin* that entered the MIM collection c.1880 presents no surface cracks either.

The "Qiulai" *qin* shows 18th-century features, and material characterization analyses as well as ¹⁴C results are consistent with the traditional practices of the *qin* makers from this period as described in written sources [3, 4]. The authenticity of this *qin* is credible. Indeed, the Qing dynasty period was rich in cultural exchanges

between China and France under the Ancient Regime. French sinophilia during the 18th Century Enlightenment is also well-known under the reign of Qianlong (1735–1796). China's tolerance toward Christianity allowed the establishment of Jesuits whose exchanges with the Académie Royale des Sciences provided information on Chinese techniques of the time. For example, the Jesuit Pierre Nicolas Le Chéron d'Incarville (1706–1757) sent a memoir to the Académie in 1760 mentioning the use of resin tree and calcined deer bones in black Chinese lacquers [43]. The sending and the studying of *qin* in the eighteenth century in France is attested. For example, the Jesuit priest Joseph-Marie Amiot (1718–1793) sent a *qin* to M. Bertin for his cabinet of curiosities [44], as reported in his correspondence with the Académie des Sciences [45]: "The first is a *Kin*¹⁴ with seven strings, unlike those of today (...). It is made of a single piece of wood".

If the "Qiulai" *qin* was made by Tang Kai and kept its original lacquer, then it was manufactured in the [1659–1699] interval, since the ¹⁴C dating results on the red lacquer provide intervals that do not include the date of 1712 carved on the back side of the *qin*. The carving of inscriptions on a *qin* traditionally took place after the instrument had been made and even played for several years.

Conclusions

The most significant findings that emerge from this study are that the *qin* rediscovered in the CNAM collection has exceptional characteristics that are consistent with current knowledge about eighteenth-century *qin* manufacture. Several aspects might contribute to the testimony of the *qin*'s authenticity: its shape, the carved inscriptions including Tang Kai's seal, the consistent ¹⁴C dating of the different materials of the *qin*, the choice of the wood, the lacquer composition and stratigraphy, while the archival documents and the absence of cracks *duanwen* 斷紋 provide additional clues testifying that the *qin* was scarcely played and well-preserved in the French collections prior to 1849. While interdisciplinary investigations on early Chinese zithers are seldom used, our results were achieved thanks to the combination of material characterization techniques, advanced radiocarbon dating technology and museum expertise confronted with early Qing dynasty written sources. This research project constituted a unique opportunity to study one of the most remarkable *qin* kept in Europe.

¹³ For example: Signatures, Inscriptions, and Markings of "Xiangpu's Treasure" Guqin (古琴) translated by Hui Fang, Dept. of Asian Art, December 2014. The Met, 2014 <https://www.metmuseum.org/art/collection/search/670501> (accessed May 16, 2021).

¹⁴ *Kin* is the name given by the Jesuit community under the Ancient Regime to *qin*.

Supplementary Information

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Additional file 1: Table S1: Conventional, calibrated and modelled ^{14}C ages obtained for the "Qiulai" qin using OxCal4.3.2 [33] based on IntCal20 [34]. Statistical results of Bayesian modelling are shown in the last four columns. **Fig. S1.** (from the top to the bottom) ATR-IRTF spectra of the finishing lacquer (b) and the black lacquer (a) with a noised signal, especially for the black layer due to the presence of inorganic elements such as copper, gypsum or aluminosilicates. The pics are relevant with lacquer spectra (database IRUG <http://irug.org/search-spectral-database>) [46]. Data were recorded within the range 4000–500 cm^{-1} using a spectrometer Nicolet 6700 equipped with a diamond ATR module (SMART endurance) and with the OMNIC software (Thermo Fisher Scientific) [47].

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Authors' contributions

MGD and SV designed the study with input from CH and AGM. CF was responsible for the loan of the object and agreed with the way the study was conducted. MGD, AGM, SV, CF are responsible for the historical and scientific documentation of the instrument. Radiocarbon and statistical analysis were performed by CH and MGD. TF prepared cross sections and performed material characterization on samples. TF and WN discussed the results and interpreted them in the context of radiocarbon dating. The global interpretation was the result of a collective thinking of all authors. MGD wrote the manuscript with input from all co-authors. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article. Raw data (including spectra) are available upon request from the authors.

Declarations

Competing interests

The authors declare that they have no competing interests.

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Additional data

Identification		Laboratory reference		Uncalibrated data				Calibrated data	Statistical modelling
Samples	ID	GifA #	ECHO #	Number of measurements	¹⁴ C activity (F ¹⁴ C ± 1 σ)	age ¹⁴ C ± 1 σ (year BP)	Chi 2	Age range with IntCal20 (calAD)(95.4%)	Resulting calibrated date [range yr AD] (95.4%)
qin_foot back side	Q1	GifA19208	ECHO 2833	2	0.967 ± 0.005	265 ± 40	1.39/3.84	1493 - 1603 (43.6%) 1608 - 1679 (38.2%) 1742 - 1752 (1.2%) 1764 - 1799 (10.7%) 1941 - ... (1.7%)	X ² -Test: df=3 T=1.010(5% 7.815) Agreement n=4 Acomb=114.1%(An=35.4%) [1458 – 1528] (46.0%) [1552 – 1634] (49.5%)
qin_pillar	Q2	GifA19209	ECHO 2834	2	0.957 ± 0.006	355 ± 45	1.15/3.84	1456 – 1640 (95.4%)	
qin_foot	Q3	GifA19210	ECHO 2835	2	0.955 ± 0.005	375 ± 45	0.06/3.84	1446 - 1530 (49.2%) 1538 - 1636 (46.2%)	
qin_wood under lacquer layers	Q5-1	GifA20230	ECHO 3480	1	0.950 ± 0.011	410 ± 90		1323 - 1356 (2.8%) 1392 - 1661 (92.5%) 1789 - 1792 (0.2%)	
qin_silk string	Q4	GifA19211	ECHO 2836	2	0.980 ± 0.005	160 ± 40	0.27/3.84	1660 - 1699 (17.8%) 1722 - 1814 (47.4%) 1835 - 1883 (10.1%) 1883 - 1889 (0.7%)	X ² -Test: df=1 T=0.248(5% 3.841) Agreement n=2 Acomb=110.9%(An=50.0%)

								1909 - ... (19.4%)	[1660 – 1699] (17.8%)
qin_red lacquer	Q5-3	GifA20363	ECHo 3738	1	0.976 ± 0.007	200 ± 50		1643 - 1710 (22.5%) 1720 - 1820 (43.6%) 1820 - 1824 (0.4%) 1832 - 1892 (12.1%) 1906 - ... (17.0%)	[1722 – 1814] (47.4%) [1835 -1883] (10.1%) [1883 – 1889] (0.7%) [1909AD - ...] (19.4%)
qin_black lacquer	Q5-2	GifA20231.1 GifA20231.2 GifA20231.3 GifA20231.4	ECHo 3481.1 ECHo 3481.2 ECHo 3481.3 ECHo 3481.4	4	0.801 ± 0.008 0.811 ± 0.008 0.768 ± 0.008 0.793 ± 0.008	1780 ± 80 1690 ± 80 2130 ± 80 1860 ± 80	16.96/7.82	30 - 528 (95.4%) 215 - 559 (95.4%) -383 - 26 (95.4%) -35 - 565 (95.4%)	

Table S1: Conventional, calibrated and modelled 14C ages obtained for the "Qiulai" qin using OxCal4.3.2 [33] based on IntCal20 [34]. Statistical results of Bayesian modelling are shown in the last four columns.

Résumé : Le travail de thèse présenté ici s'inscrit dans une stratégie générale initiée par le Musée de la musique de Paris visant à intégrer des approches archéométriques dans les efforts de documentation des instruments de musique à la fois objet d'art et d'usage, témoin matériel des exigences musicales et culturelles environnantes. De fait, les instruments de musique sont rarement associés à des sources écrites précises, ayant été produits selon des pratiques artisanales à transmission orale. L'objectif de cette recherche est d'explorer la faisabilité et les limites d'adaptation de deux techniques avancées, largement appliquées aux archéomatériaux: i- la géochronologie ^{14}C (datation) et ii- la géochimie isotopique du strontium (traceur d'origine géographique), aux problématiques spécifiques des collections muséales d'instruments modernes, datés essentiellement des 17^e et 18^e s. La recherche s'est concentrée sur les vernis, portant les traces de l'histoire matérielle des usages, plus particulièrement à base d'huile de lin/colophane (Échard, 2010; Tirat, 2015). Le corpus d'étude a été étendu au mobilier et aux hippomobiles du début du 18^e s. En effet, les vernis originaux huile de lin/colophane y ont été conservés et les problématiques d'usage s'y trouvent aussi présentes (entretien, restauration, revernissage, etc.). Le corpus comprend également des cordes de boyaux anciennes, celles-ci témoignant de l'usage musical de l'instrument de musique. Le partenariat entre le Musée de la musique de Paris et le Laboratoire des Sciences du Climat et de l'Environnement (LSCE) combine l'expertise indépendante du musée aux technologies les plus pointues pour les mesures ^{14}C (ECHO MICADAS) et isotopiques du strontium (MC-ICP-MS, Neptune). Ce travail repose ainsi sur la combinaison de ces deux approches à la documentation historique et à une large palette d'outils d'analyse en caractérisation des matériaux.

Le volet géochronologie ^{14}C de cette recherche a débouché sur le développement de protocoles d'échantillonnage et de traitements chimiques permettant d'analyser les matériaux du patrimoine culturel selon leur nature. L'environnement chimique complexe et composite des revêtements nécessite, en effet, des développements méthodologiques pour extraire le "bon" carbone à dater. L'étude a également apporté des éléments ayant permis d'approfondir la connaissance sur les objets analysés et leurs usages, comme l'impact de certaines restaurations, le réemploi de matériaux ou la nature de certains ingrédients.

Le volet d'étude de provenance par isotopie du strontium s'est concentré sur une étude de faisabilité pour la colophane. La conservation de la signature $^{87}\text{Sr}/^{86}\text{Sr}$ depuis le substratum jusqu'à la résine de pin distillée ou colophane a été validée par les analyses isotopiques sur un corpus de couples sol/résine et de trios sol/résine/colophane d'origine connue. Une sélection de colophanes du marché actuel fournit des mesures du ratio $^{87}\text{Sr}/^{86}\text{Sr}$ cohérentes avec les cartes géochimiques.

Cette thèse met en évidence l'état d'avancement des adaptations méthodologiques de la géochronologie ^{14}C et de la géochimie isotopique du strontium appliquées aux vernis historiques du 17^e et du 18^e s. Elle montre la possibilité de surmonter des écueils tels que la taille de l'échantillon pour la datation ^{14}C , en respectant l'intégrité des objets du patrimoine, ou la réduction du niveau de contamination en strontium pour les mesures isotopiques sur les résines de pin. Elle a fait l'objet de trois publications (Durier et al. 2019 Radiocarbon, Durier et al. 2021 Heritage Science, Durier et al. 2022 Technè). La recherche ouvre de nouvelles perspectives pour aborder les questions de la contrefaçon, de la retouche, des interventions d'entretien ou de restauration sur les instruments de musique, et pour mettre en évidence des liens entre les anciens centres de production de résines naturelles et les centres historiques de fabrication de violons.