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Tailored Compound Specific Carbon Isotopes Analysis in Heritage Science

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Abstract: Radiocarbon dating has long been a cornerstone of archaeological science, offering a reliable method to determine the age of organic materials. Yet when applied to cultural heritage objects, traditional bulk analysis methods often fall short. Our research, supported by an SNSF Ambizione program, seeks to overcome these limitations by shifting the focus from bulk materials to individual molecules. We aim to untangle the mixed carbon sources encountered in heritage materials through compound specific approaches and further target the color of an object, *i.e.* natural organic dyes and pigments. This perspective opens new avenues for understanding the chronology, provenance, and material history of cultural heritage objects. The implementation of compound specific radiocarbon analysis (CSRA) and compound specific isotopic analysis (CSIA) in heritage science demands not only analytical precision but also an uncompromising approach to exogenous carbon contamination control. Herein, we describe our current efforts in developing color specific carbon isotopic analyses that address this challenge.

Keywords: Colorants · Compound specific analysis · Heritage science · Radiocarbon dating · Stable isotope analysis

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development of compound specific isotopic analysis approaches tailored to the needs of heritage science.

1. Introduction

Determining when and where artworks were produced lies at the core of Heritage Science. Ascribing a production date to artifacts allows researchers to place them within their cultural and historical context, further refining our understanding of technological evolution. Provenance studies, meanwhile, shed light on material sourcing, manufacturing practices, and trade networks that shaped economic and artistic exchange. Overall, answering questions of chronology and origin is crucial for understanding the social, cultural, and technological developments of past societies. Until today and despite many limitations, material identification by non-invasive and non-destructive techniques remains one of the preferred methods to determine the production date of an artifact. By comparing the materials present with their first documented use, a *terminus post quem* date may be established. Limitations of spectroscopic methods include low specificity of results and complex data interpretation due to overlapping responses from the analytes and matrix, reducing confident identification. Additionally, many materials, such as lead white or madder lakes, for example, have been in continuous use across the globe since Antiquity and thus offer limited chronological and geographical information. In such cases, absolute dating and provenance techniques become essential to refine or confirm hypotheses.

1.1 *Radiocarbon (^{14}C) Dating and Stable Isotope Analysis in Heritage Science*

Radiocarbon (^{14}C) dating, first developed by Willard F. Libby in 1946, allows the determination of the age of organic materials by measuring the decay of ^{14}C, a radioactive isotope formed in the atmosphere and incorporated into living organisms.[1] While chronological questions are key in heritage science, the destructive nature of ^{14}C measurements, and most importantly the large sample size requirements hindered its application. In its early years, the method called for sample sizes in the order of grams of material, as physicists relied on detecting the weak radiation emitted by decaying ^{14}C atoms.[2] The advent of accelerator mass spectrometry (AMS) in the 1970s enabled direct counting of ^{14}C atoms,[3,4] reducing sample requirements to the milligram scale. With gas ion sources introduced in the late 1980s, samples no longer needed to be converted to graphite as carbon dioxide could be used directly,[5,6] micrograms of carbon became measurable, resulting in an overall downscaling by six orders of magnitude.

In turn, thanks to these technological advancements, new avenues of research became possible including heritage science. While applications initially focused solely on the support material,[7–9] alternatives were sought in dating the natural organic binder as it constitutes a better proxy to date the creation of the artwork itself.[10] While a proof of principle was provided as early as 1972 by Keisch and Miller on a 100 mg scale,[11] direct dating of the natural organic binder recently became feasible by analyzing paint samples weighing less than 10 mg and as small as 160 µg.[10,12] Similarly, the possibility of dating microsamples containing lead white pigment was recently put forward.[13–15] Even though chemically classified as an inorganic species, the historical manufacturing processes of lead white results in the incorporation of atmospheric CO_2 into the crystal lattice, which makes it a good proxy for radiocarbon dating. Several lead white containing matrices were investigated, from ancient cosmetics,[16] to mural[17] and oil paintings[13,14,18,19] and polychrome sculptures.[20,21] Nonetheless, while sample size is no longer an issue due to technological advances, a recurring problem is sample heterogeneity. Indeed, successive layers of chemical complexity accumulate starting from an object's creation and continuing with its use, deterioration, and restoration. These secondary organic sources result in measurable biasing effects towards older or younger ages, depending on their composition.[22] Materials responsible for such isotopic contamination have been previously attributed to the presence of conservation materials such as paraffin,[23] natural gums and beeswax,[24] Paraloid B-72,[25] PVAc,[20] or carbon-containing colorants such as carbon black[20,26] or synthetic organic pigments.[27] The application of radiocarbon dating to painted artworks is therefore hindered by sample preparation limitations, which are currently not able to address the chemical complexity of cultural heritage materials.

Isotopic analyses beyond radiocarbon dating are increasingly valued in heritage science for the insights they offer into the provenance of materials.[28] In particular, stable isotopes refer to the isotopes that do not undergo radioactive decay or have half-lives many orders of magnitude larger than the age of the Earth.[29,30] Lead white is a common example for both heavy and light isotope analysis. Lead isotope distribution allows the study of the processes involved in the production of lead pigments, providing insights into sourcing, manufacturing and artistic practices.[31] Similarly, ^{14}C and δ^{13}C measurements provide information about the chronology and carbon sourcing for the white pigment production, either independently,[32] as does coupling lead isotope analysis on the cation and ^{14}C analysis on the anion.[19] Besides C, isotopic ratios of light elements such as H, N, O and S may also provide source information as they vary depending on environmental factors, such as climate, geology, soil pedology, and biological processes. In broad terms, while the isotope ratios of ^{13}C/^{12}C and ^{15}N/^{14}N relate to the growth climate and agricultural practices, the ratio of ^{34}S/^{32}S is reliant on geology, volcanic activity, distance from the sea, and some anthropogenic activity. The measured ratios of ^{18}O/^{16}O and ^{2}H/^{1}H reflect the isotopic composition of the water in the source region.[33] The development of the magnetic sector mass spectrometer specific to isotope studies by Alfred O. Nier in the 1940s expanded the scope of application by making the instrumentation more accessible for more laboratories and research fields.[34,35] Today, it is a versatile method used heavily in highly diverse fields, such as food safety, pharmaceutical research, archaeological studies, and environmental science.[36–38] However, in the context of heritage science, it suffers from the same limitations as bulk radiocarbon dating analysis due to exogenous contaminations, causing isotopic biasing effects.

1.2 *Knowledge Gap*

Separating intermingled carbon sources for accurate isotopic measurements remains one of the most challenging aspects in the complex matrices that compose cultural heritage objects. Yet we believe it is achievable through the development of compound-specific approaches, based on the isolation of targeted biomarkers using preparative chromatography. Compound specific radiocarbon analysis, commonly known as CSRA, was first developed in 1996 by Eglinton *et al*. for the analysis of soil and sediment matrices to overcome isotopic heterogeneity caused by exogeneous carbon contamination.[39] Initially developed on *n*-alkanes and fatty acids,[40–42] the scope of CSRA has now been expanded to other molecular classes such as amino acids[43] and phenols,[44,45] all extracted from environmental matrices. Interestingly, several of these markers are also commonly analyzed in heritage materials, particularly in painted materials. While oil-based binders, *i.e.* fatty acids, are arguably the most commonly found material since the start of the Renaissance, artworks have been produced using a variety of materials since Antiquity, including wax (*n*-alkanes), egg and glue (proteins), as well as plant resin and gum (polysaccharides).[46] Despite many similarities in the respective chemical compositions, no CSRA applications have been developed to address the complexity of heritage material matrices.

The closest analogy is found in archaeology, where fatty acids extracted from cooking vessel fragments are used as dating proxies. While the first trials lacked accuracy and precision,[47,48] further optimization by Casanova *et al*. allowed for the use of preparative gas chromatography (pcGC) to isolate methyl palmitate and stearate.[49–51] The latter two are key molecular markers in natural oil binders, and their successful isolation in archaeological contexts supports the development of analogous compound-specific approaches in heritage science. Interestingly, stable carbon isotope analysis has been used in conjunction with radiocarbon measurements for combined dating and provenance determination of lipids using the equivalent of CSRA for stable isotope analysis, known as compound specific isotope analysis (CSIA).[52] The commercial production of gas chromatography/combustion/isotope ratio mass spectrometry (GC-C-IRMS) in the early 1990s laid the way for an increasing number of CSIA studies, particularly in the geochemical, palaeoecological, and archaeological communities for past environment and human life reconstruction.[53–56] Most importantly in a heritage science context, CSIA was used for the first time by Geddes da Filicaia *et al*. to ascribe the geographical origin of carminic acid, a vivid red dye extracted from cochineal insects.[57] The success of these methods in archaeology provides a robust foundation for the development of both CSRA and CSIA strategies in cultural heritage science.

1.3 *Project Vision*

Among material typologies found in historical objects, colorants occupy a central role in historical materials, having conveyed emotion, symbolism, and status since Prehistory.[58] Found in paintings, textiles, sculptures, and varnishes, they offer rich insights into material culture but their analysis is complicated by limited sampling possibilities, low concentrations, degradation processes, and matrix heterogeneity. Radiocarbon and stable isotope analysis hold great promise in this field, yet until today, lead white remains the only pigment targeted for radiocarbon dating and stable isotope analysis. Before the invention of the first synthetic dyestuff mauveine in 1856,[59] all dyes were derived from natural sources, including roots, berries, flowers, heartwood, lichens as well as snails and insects. The diversity in dye sources resulted in a wide variety of chemical structures, including anthraquinones, flavonoids, tannins, carotenoids, and anthocyanins.[60] Because these molecules not only incorporate atmospheric $^{14}CO_2$ during the growth phase of their source organisms but also isotopic signals from their geological environment, they hold great potential for radiocarbon dating and stable isotope analysis.

Within our SNSF Ambizione project we aim to target the molecules responsible for the object's color. This is founded on the principles that; i) the carbon backbone of natural organic dyes stores a wealth of information regarding its source and origin, and ii) this information may be retrieved by capitalizing on compound specific analysis as opposed to bulk sample analysis. Similar compounds which were the target of CSRA in many environmental applications can be found in heritage materials and thus present valuable ^{14}C candidates for dating of art objects. The overarching goal of this project is to pioneer the development of compound specific isotopic analysis approaches, specifically CSRA and CSIA, tailored to the needs of heritage science. By targeting both the colorants and the natural organic binder in complex matrices, insightful results regarding the artefact's narrative will be gained.

2. Methodological Framework

2.1 *CSRA Methodology*

Typically, CSRA introduces targeted chemical extraction protocols followed by a chromatography step coupled to a preparative system enabling the purification and isolation of compounds, prior to radiocarbon dating by AMS. For this, pcGC or liquid chromatography (prep-HPLC) techniques are used depending on the physico-chemical properties of the analyte. As only a fraction of the compound of interest is isolated for dating, the low abundance of targeted analytes in the matrix poses a major challenge for CSRA, often causing analyzed carbon masses to fall below 100 µg. While permitted by recent advances in AMS technology, including system miniaturization MICADAS and the coupling with versatile gas handling interfaces,[61,62] these small sample sizes are particularly vulnerable to biases from exogenous carbon contamination (C_{Ex}). The latter can be split according to the various steps encompassed by the CSRA workflow, which each contributes in various extents to C_{Ex} (Eqn. 1):

$$C_{Ex} = C_{Matrix} + C_{Chem} + C_{Chrom} + C_{EA-AMS} \quad (1)$$

C_{EA-AMS} is the background levels from the sample combustion and ^{14}C measurement. Carbon contamination from preparative chromatography purification and post-isolation transfer are accounted for by C_{Chrom}. C_{Chem} is related to chemical extraction and finally any remaining impurities originating from the sample matrix are grouped under C_{Matrix}. Whenever possible, large samples, usually > 200 µg of C, are processed to render exogeneous contamination negligible, with the required carbon mass depending on the magnitude of C_{Ex}.[39,49] While processing larger samples is feasible for environmental matrices, this approach is not suitable for heritage materials due to ethical sampling concerns.

To ensure high accuracy measurements of small samples, it is crucial to accurately assess and correct for C_{Ex} from the measured (C_m) carbon. Two values are required for this, the mass of contamination m_{Ex} and its normalized isotopic ratio $F^{14}C_{Ex}$ (Eqn. 2). The former can be approached though process blank measurements, while the latter is most readily measured through constant contamination modelling.[63–66] The magnitude and uncertainty on both m_{Ex} and $F^{14}C_{Ex}$ affect the precision on the derived sample age (C_S) and must be accounted for through error propagation.[65–67] A large importance has therefore been put on careful monitoring and minimization of all sources of exogeneous carbon.[49,68,69]

$$C_M = C_S + C_{Ex} = \sum_i F^{14}C_i * m_i \quad (2)$$

2.2 *CSIA Concept Validation*

Currently, the pinpointing of dye origin is limited to the identification of plant-specific molecular markers in combination with archival research.[70] Focusing on indigo, dye analysis only provides lacunar and sometimes misleading conclusions. For example, synthetic indigo only contains indigotin, naturally sourced indigo commonly contains both indigo and indirubin, along with isatin. However, the absence of the latter two does not necessarily confirm a synthetic source, as their low concentration may cause them to go undetected, especially in poorly conserved materials. Hence, an absolute criterion for determining if indigo is of natural or synthetic source based on chromatographic data remains elusive.[71,72] A recent study by Pauk *et al*. offers a more robust differentiation using ion mobility spectrometry combined with chemometrics.[73] However, the scope remains limited to plant-derived sources from Europe, India, and the Middle East, excluding synthetic indigo. While many current stable isotope studies in cultural heritage focus on the textile substrate,[74,75] recent CSIA studies targeting the dye itself have shown promise

in distinguishing Mexican versus European cochineal based on different $\delta^{13}C$ values.[57] The results of this approach provide the preliminary foundation for the proposed project, demonstrating the application potential of CSIA for dye analysis. Moreover, differences could be highlighted between dye and substrate supply modes, either local or imported, depending on the availability of each material. For dye purification several approaches can be adopted, from HPLC isolation followed by offline IRMS analysis or online GC-C-IRMS measurements requiring dye derivatization as performed by Geddes da Filicaia *et al*. for carminic acid.[76]

3. Preliminary Results and Insights

3.1 *Challenges and Contamination Control in CSRA*

While CSRA approaches offer the key for untangling the variety of carbon sources in cultural heritage materials, their implementation demands not only analytical sensitivity but also rigorous control over contamination. The proof-of-principle of the approach in coupling dye analysis with CSRA was demonstrated on anthraquinone-derived red dyed wool substrates.[77] The associated ^{14}C constraints within the different steps of the methodology covering the chemical extraction, chromatographic separation, and final ^{14}C analysis were exemplified in a perspective paper.[78] The most straightforward way to monitor the overall contamination (C_{Ex}) is to quantify background carbon levels through systematic process blank testing, from the final packing of the purified fraction in vessels prior to combustion, going back through the chromatographic elution profile and chemical extraction. Fig. 1 displays the measured carbon mass for different sets of processed blanks, allowing a direct estimate of the size of C_{Ex}.

At the elemental analyzer (EA)-AMS interface, the choice of the sample container prior to combustion was found to play a decisive role. Different materials and shapes can be purchased to better fit the sample typology. Here, as the targeted analytes are recovered as solutes before being evaporated to dryness, the use of cylindrical shaped vessels is preferred. Both types were subjected to pre-cleaning as suggested by Welte *et al*.: tin cups were cleaned using DCM and the aluminum cups were pre-combusted at 550 °C.[68] As shown in Fig. 1, aluminum capsules were shown to carry a lower carbon footprint compared to tin vessels, with values of 0.3 ± 0.1 and 1.6 ± 0.2 µg C, respectively. While the aluminum results are in good accordance with previous findings, the tin vessels showed higher background carbon than expected and were found to be linked to a specific contaminated batch.[68,69,77]

Dye analysis by HPLC is almost exclusively conducted on a reversed phase based C18 column, which is eluted by a gradient of water and methanol or acetonitrile as an organic eluent adjusted with an acid phase modifier.[79,80] Fig. 1 is quite revealing in the C_{Chrom} contribution, as all tested columns induced slight leaching of silica-bonded constituents, resulting in detectable column bleed during chromatography. On average the Zorbax Eclipse C18 (4.6 × 100 mm, 3.5 µm) had the lowest contribution with 5 ± 1 µg C. To be noted, columns were tested with tin cups, thus the actual C_{Ex} is to be adjusted on average by 1–2 µg. Among the tested acids, trifluoroacetic acid (TFA), despite the lowest concentration and high volatility, was by far the worst choice. Phosphoric acid (H_3PO_4), attractive in principle because it is carbon-free, proved problematic in practice: the commonly available 85% reagent introduces non-negligible impurities, and its high boiling point (> 150 °C) resulted in residual deposits that corroded the metallic cups after drying. In comparison, formic acid (FA) was found to offer the best compromise between chromatographic features such as optimal peak shape, resolution and introduced exogenous carbon. Our results highlight the necessity of routine blank assessments and the careful selection of materials and reagents. By optimizing all the aforementioned steps, specifically by selecting aluminum cups, the Zorbax column, and formic acid, we achieved a significant reduction in C_{ex}, yielding on average 3 ± 1 µg C, consistent with results gained in the pilot study.[77] This also agrees with our earlier observations, which showed that the major exogeneous contribution comes from C_{Chrom}. These results are also consistent with data obtained by other groups worldwide using liquid chromatography approaches in their CSRA methodology, who report between 1 and 8 µg C.[81–84]

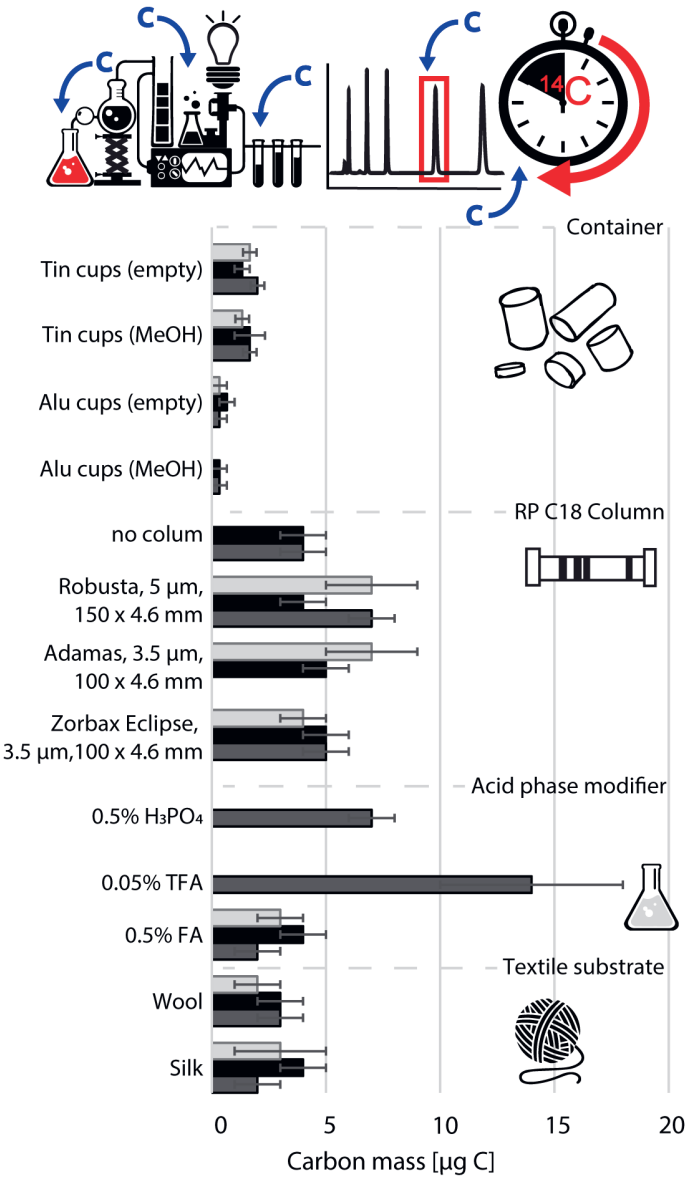

Fig. 1. Measured exogenous carbon introduced at different stages of the CSRA workflow, separated by horizontal dashed lines. The column tests were conducted in tin cups, whereas the acid phase modifier tests were run using aluminum cups. Triplicates were conducted for each parameter investigated and repeated over different sequences as given by the different shades of grey.

Ongoing work focuses on the investigation of additional chromatographical parameters which have been shown to have an impact on C_{Chrom}, such as the volume of eluent collected, *i.e.* number of injections and collection window size,[85] as well as the ratio between the aqueous and organic mobile phases.[81,82] These factors are crucial in determining how many markers should be isolated in a given sample. The improvements in precision acquired by purifying larger quantities of carbon could in certain cases be negated by a concurring increase in C_{Chrom}. Additionally,

it is possible to isolate and date multiple markers pertaining to the same material separately, similar to the approach of Casanova *et al*., for palmitic and stearic methyl esters in pottery shards, which enables internal validation of the two radiocarbon dates, albeit at the cost of precision due to lower carbon masses per isolated compound.

Focusing on anthraquinone-derived red dyes such as alizarin and purpurin, we assessed both C_{Chem} and C_{matrix}, when extracting the dyes from dyed wool yarns (Fig. 2). Naturally dyed textiles were chosen as the starting point as they represent the simplest substrate–matrix system, and prior work had already demonstrated the compatibility of sequential dye analysis and ^{14}C dating.[86] Although, current consensus in dye analysis favors the use of mild procedures, HCl-based treatments are known to produce higher dye yields, but also lead to degradation of the substrate.[79,87] Adjusting the acid concentration from 37% to 2% emerged as the key factor, offering the best compromise between dye recovery and preservation of the textile matrix. As illustrated in Fig. 2, wool treated with concentrated HCl (37%) displayed elevated background UV-Vis signals and clear signs of fiber degradation, whereas treatment with dilute HCl (2%) maintained low background levels and preserved the integrity of the matrix. Processed blanks of undyed wool and silk yarns yielded values comparable to HPLC blanks, confirming that C_{Matrix}+C_{Chem} are negligible contributions to C_{Ex}, with C_{Chrom} remaining the dominant source of exogenous carbon.

These findings cannot be extrapolated to all heritage materials, as the CSRA methodology must be adapted to both the chromophore and its substrate. In dyed textiles, a relatively simple hydrolysis is often sufficient to release the dye with minimal interference. By contrast, painted substrates are significantly more intricate, as the dye is precipitated as a lake and is embedded in the organic binder matrix as illustrated in Fig. 3. Here, direct transmethylation of triglycerides must be combined with dye hydrolysis in methanolic HCl, followed by liquid–liquid extraction to separate binder and dye. This dual approach allows us to successfully analyze the dye by HPLC and the oil binder by GC. These examples underscore the necessity of tailoring CSRA protocols to the material substrate, with textiles offering relatively straightforward extractions, and multi-component paint systems demanding more elaborate workflows to isolate pure fractions. Ongoing work focuses on optimizing chromatographic purification and quantifying all the contributions to C_{Ex}. If C_{Chrom} and $C_{EA\text{-}AMS}$ are expected to be identical between textiles and paint samples, the differences in matrix composition and chemical extraction could differ significantly.

A further challenge in the development of CSRA strategies is finding suitable standards of known complementary ^{14}C content for constant contamination modeling. Given the wide diversity of natural organic dyes found in artworks, our work initially focused on red anthraquinone dyes, such as alizarin and purpurin. These compounds, originally extracted from the roots of the madder plant of the Rubiacea family, are also commercially available as petroleum-derived synthetic analogues.[88] Chemically indistinguishable, the compounds differ in their respective isotopic composition, providing readily accessible pairs of ^{14}C-modern and ^{14}C-depleted materials. In contrast, commercial production of carminic acid, for example, still relies on extraction of the precious dye from harvested cochineal insects, despite the successful chemical synthesis of carminic acid in the 1990s,[89] thus underscoring its enduring economic and cultural value, as well as the complexity of synthesis in the laboratory. As such, commercial carminic acid carries solely a modern biomass signature. As a result, ongoing work is to synthesize our own ^{14}C depleted standards, following a total synthesis approach using petroleum based starting materials.

3.2 *Proof of Principle for CSIA of Indigo Colorant*

Before being synthetically manufactured on a large scale by BASF in 1897, indigo blue was historically produced on a commercial scale from four biological sources: *Isatis tinctoria L.* (woad), *Indigofera tinctoria L.* (true indigo), *Persicaria tinctoria* (Aiton) H. Gross (Japanese indigo, dyer's knotweed), *Indigofera suffruticosa* Mill, each species being cultivated in specific regions of the world, *i.e.* Europe, Central Asia and India, Southeast Asia and Japan, central and south America, respectively.[70,90]

Preliminary data gained in the frame of a pilot study shows that based on the compound's ^{14}C isotopic signature, the source of carbon can be determined (vertical spread, Fig. 4), either natural ($F^{14}C \sim 1$) or synthetic from oil or coal tar origin ($F^{14}C \sim 0$). Carbon isotopic analyses ($\delta^{13}C$) typically show a depletion in ^{13}C with respect to atmospheric CO_2, ranging between –25 to –35‰ as a result of plants using different photosynthetic pathways.[91,92] Within the Ambizione project, we hope to show that a horizontal spread, *i.e*. variations in $\delta^{13}C$ values may be used as a new metric to allocate a geographical origin of the dye and so appoint the potential plant source. The distinct geographical origins of the four indigo sources means that identification of the species used would lead to an increased understanding of historical civilizations and their interconnections. Development of analytical techniques that can differentiate between the different dye sources would facilitate a deeper understanding of trade relations, fashion,

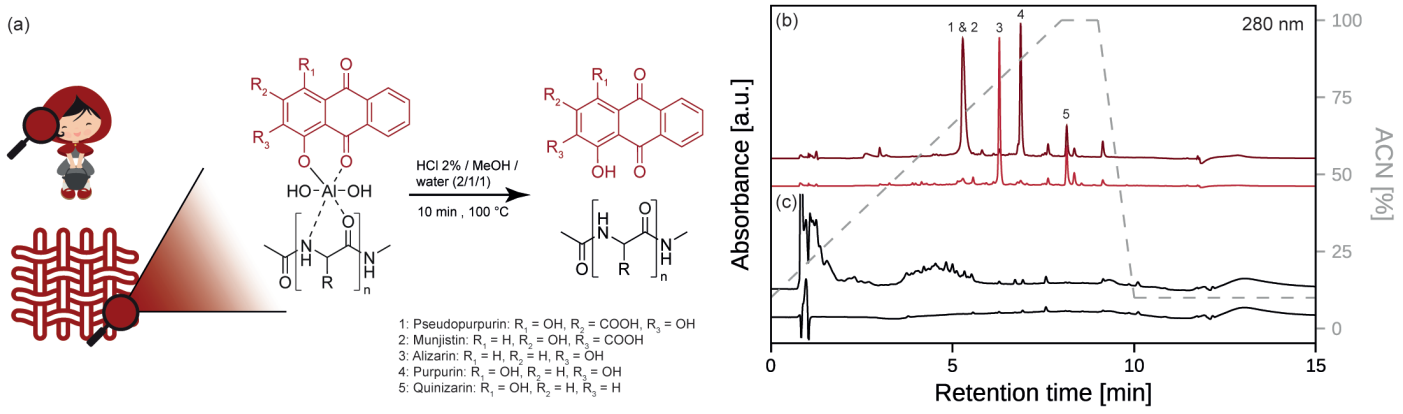

Fig. 2. (a) Optimized chemical extraction conditions and respective HPLC-DAD (DAD = diode array detector) chromatograms of hydrolyzed extract of wool yarns dyed with (b *Rubia cordifolia L*. (dark red, top) and *Rubia tinctorum L.* (lighter red, bottom) (c) comparison of undyed wool fibers extracted with an HCl 37% based solution (top) and HCl 2% (bottom).

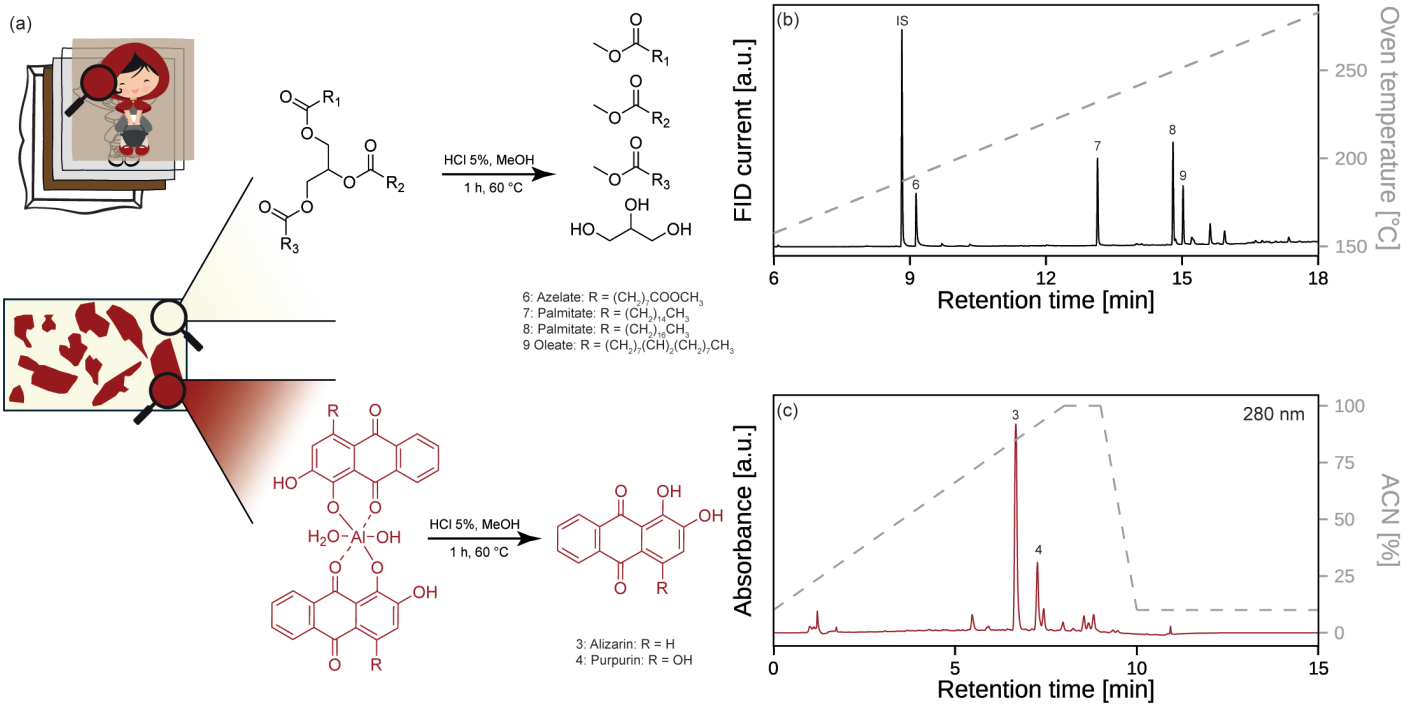

Fig. 3. (a) Optimized chemical extraction conditions for simultaneous triglyceride transesterification and lake pigment hydrolysis; (b) GC-FID chromatogram (FID = flame ionization detector) of a fatty acid methyl esters (FAMES) mixture extracted from a linseed oil paint film, using methyl laurate as an internal standard (IS); (c) HPLC-DAD chromatogram of the extract of hydrolyzed *Rubia tinctorum L.* lake pigment.

and manufacturing advancements of past societies. This is an important part still lacking in dye analysis and it is what this project hopes to address by the application of stable isotope analysis. One of the main challenges of this project will be to investigate the large number of variables that may affect the measured isotope ratio. Not only can isotopic fractionation occur during the sample preparation step, but potential fractionation effects throughout the lifetime of the object will be assessed. This includes the impact of the processing of the plant into indigo powder, the dye bath conditions, the textile fiber used, and the use and storage of the historical object in its environmental context. Eventually, the goal of the project is to expand the application of CSIA to dyestuffs beyond indigo, such as mordant dyes like madder. The diverse processing and dyeing methods used in natural dyeing means that fractionation effects which impact isotopic ratios will have to be understood for each individual dye.

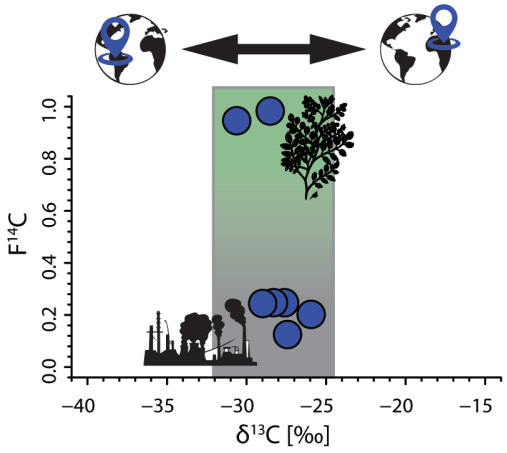

Fig. 4. Plot of $^{13}C/^{12}C$ ratio *vs* $^{14}C/^{12}C$ ratio of indigo samples of natural and synthetic origin. The measured $F^{14}C$ values show a distinct vertical spread making it possible to distinguish between plant and synthetic samples.

3.3 *Application Scope*

By targeting naturally dyed textiles, the goal is to establish the methodological parameters necessary to produce the first ^{14}C dates on natural organic dyes and pigments. This is achieved by isolating their specific ^{14}C signature from the textile matrix, leading to their establishment as dating proxies. From red anthraquinone derivatives, future work will expand the development of CSRA strategies to yellow and blue chromophores, which owing to different compound classes, flavonoids and indigoids respectively, require alternative extraction protocols and adapted chromatographical isolation Therefore, C_{Chem} and C_{Chrom} will need to be tailored not only to the matrix but also to the targeted chromophore. Building on experience gained from textile and linseed oil paint substrate matrices, the approach is to be extended to other heritage material matrices. Drawing on advances in art technology research for separating individual paint components, and building on two decades of CSRA experience, we are now only one step away from being able to radiocarbon date not only natural organic dyes and pigments, but also lipids, waxes, resins, and proteinaceous molecules, all from within the same microsample.

Our methodological development has so far concentrated on organic materials preserved in well-maintained objects, such as those held in museum collections, where materials remain in relatively good condition and close to their original aspect. In archaeological contexts, however, such ideal preservation is the exception rather than the rule. For example, archaeological textiles are rarely preserved, as organic fibers are highly susceptible to decay. In some cases, exceptional preservation can occur through mineralization, where morphological information is preserved by the growth of mineral phases formed from metal cations from adjacent metal artefacts. In temperate burials, bronze objects typically corrode to form copper carbonates such as malachite

($Cu_2(OH)_2CO_3$) and azurite ($Cu_3(OH)_2(CO_3)_2$). At Le Paradis (Creney-près-Troyes, Aube, France), numerous mineralized textiles were discovered and analyzed during Clémence Iacconi's doctoral work.[93,94] We hypothesized that these copper carbonates could serve as 'time capsules' for radiocarbon dating, analogous to lead white pigment. Optimized thermal decomposition released CO_2 suitable for ^{14}C analysis, which yielded dates between 400–800 BCE, consistent with the Iron Age context.[95] Complementary stable isotope analysis combined with the ^{14}C results clarified the events being dated, revealing environmental carbon signatures from early organic decay in the burial context. This work introduced the concept of 'adjacent dating', where carbonate corrosion products provide chronological information on associated organic materials. The physico-chemical processes underlying carbonate nucleation and growth, and textile preservation will now be further investigated with a multimodal tomographic approach combining X-rays and neutrons (On going SNSF Spark project nr. 229047).

4. Conclusions

Our group's research endeavor focuses on compound specific carbon isotope analysis, which we believe will revolutionize the application of both radiocarbon dating and stable isotope analysis in heritage science. The challenge resides no longer in the nuclear physics realm, but in the laboratory in the chemist's hands. Our aim is to target the molecules responsible for an artifact's color, focusing on the separation, identification, and quantification of these compounds before conducting isotopic analysis. Not only will the age of natural organic dyes and pigments be revealed by ^{14}C dating but their source apportionment may also be inferred on the basis of stable isotope analysis. The goal is to provide new evidence contributing to the narrative of the object's creation taking advantage of the multiple carbon sources it contains, which may further shed light on social, economic, and cultural aspects.

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