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Case study

The three-tone system in Sant Climent de Taüll wall paintings: An imprint of medieval treatises

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ABSTRACT

Medieval texts describe the use of the three-tone system as a pictorial procedure characteristic of Romanesque art to represent shape and volume. Some Medieval art treatises provide detailed instructions of its application, using specific names for each of the carnation colours: *membrana* (mid-tone or base colour), *rosa* and *posc* (darker) and *lumen* (lighter). In this study we have verified its use and application by analysing the mural paintings of the central apse of the church of Sant Climent de Taüll (Catalonia), currently on display at the Museu Nacional d'Art de Catalunya. A combination of microanalytical techniques, micro-infrared spectroscopy (μFTIR), synchrotron-based micro-X-ray diffraction (μSR-XRD), Scanning Electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), and Optical microscopy (OM), provided precise information on the composition and distribution of the compounds in the sequence of micrometric layers. We have identified the use of up to eight different pigments carefully mixed, to obtain a variety of tones in accordance to the recipes given in the Theophilus' *De diversis Artibus* and the *Hermeneia* (Byzantine pictorial tradition). The inner layers, painted directly on the still wet lime mortar, show the typical carbonation microstructure of *fresco*, while the surface layers for the contours of geometric decorative elements and figures which required longer working times, were applied *al secco*.

1. Introduction

Many of the compositional and colour application procedures of Roman art introduced by Vitruvius in *De Architectura* [1] were subsequently reproduced in numerous medieval manuscripts, although they were often transformed into practical canons or workshop rules and adapted to the customs and preferences of the time [2,3]. If these recommendations and formulations were systematically transmitted from master to disciple during the artist's training process, they should be reflected in the paintings of the conserved artworks.

Medieval treatises devoted exclusively to wall paintings do not exist or at least are not preserved. Conversely, wall paintings are only mentioned in some of the chapters, for example in chapter XV of *De Diversis Artibus* by Theophilus Presbyter (12th century) [4,5] or in third book of the Montpellier treatise, *Liber diversarum arcium* (c. 1300) [6,7]. These texts exemplify the pragmatic and functional character of medieval books with regard to painting and drawing. In addition, subsequent texts such as *Il Libro dell'arte* by Cennino Cennini (late s. XIV) [8,9] compile some enduring detailed medieval practices, or older texts, like the Greek text *Hermeneia*, of which only 18th century copies (e.g. that of Dionysius of Fourna, the first complete, extensive and well-structured text) have survived, give very specific recipes of the apparently unchanged Byzantine pictorial tradition [10].

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Table 1
Summary of the three tones described in the treatises and comparison with the composition determined by our analysis of the wall paintings of Sant Climent de Taüll.

	TONE	COLOUR TERMINOLOGY	TREATISES	COMPOSITION DETERMINED
CARNATION	Mid-tone	*Membrana*	**Theophilus' *De Diversis Artibus*** Flash colour on a wall is composed of yellow ochre, vermilion and chalk-white, and the shadow-colour for flesh, the rose, and the highlights are made as above [4 p.13]. ***Hermeneia*** Take drams of white for working on walls and drams of ochre of Thasos and drams of bole and grind them carefully on a marble slab and you will get fine flesh colour [10 p.14].	-Yellow ochre (goethite and phyllosilicates) -White (calcium carbonate, gypsum, anhydrite) -Red (haematite)
	Dark	*Rosa*	**Theophilus' *De Diversis Artibus*** Then mix with the plain flesh colour a little vermilion and a little red lead and prepare the colour which is called rose [4 p.6].	-*Membrane* -Minium -Cinnabar
		Posc	**Theophilus' *De Diversis Artibus*** Mix with it *[membrane]* some green earth, and red (which is burnt from ochre) and a little vermilion [4 p. 5–6]. When you have mixed the flesh-colour pigment and have laid in the faces and nude bodies with it, mix with it *prasinus*, the red that is burnt from ochre, and a little cinnabar, and so make shadow pigment [5]. ***Hermeneia*** Take drams of terraverte, drams of dark ochre, drams of lime-white for working on walls, and drams of black [10 p.14].	-Membrane -yellow ochre + black, possibly corresponding to *prasinius* -Iron oxide and cinnabar
	Light	*Lumen*	***Hermeneia*** Later put white on top of the same flesh painting with discretion to make it lighter [10 p.8]	-White (calcium carbonate, gypsum, anhydrite)
RED	Mid-tone	Orange red	**Theophilus' *De Diversis Artibus*** Then mix a little red lead with vermilion and paint the first light areas [4 p.10].	-Red ochre (phyllosilicates, iron oxide and quartz) -Haematite (iron oxide) -Minium -Cinnabar
	Dark	Purple red		
	Light	Red		

Medieval writings describe a pictorial procedure which has become a characteristic trait of Romanesque and Byzantine [11] art: the use of three-tone system to represent shape and volume. It consists of creating a mid-tone as a base colour layer (*miscere*), on which darkness-increased (*incidere*) or lightness-increased (*matizare*) layers are added to create the effect of shadow and light, respectively [12]. Although its use in wall paintings is not always mentioned thoroughly or explicitly, medieval texts describe the systematic application of this method to various bidimensional supports and media. In fact, the treatises only describe the main particularities in relation to the use of lime, but more extensive explanations refer to other supports or techniques. In the following, we examine whether this procedure was followed and how it was applied to wall paintings.

The human figure and, specifically the face, was considered the most important element in pictorial compositions. For this reason, medieval art treatises provide detailed instructions for its depiction and use specific names for each of the colour combinations of the carnation: *membrana* (mid-tone or base colour), *rosa* and *posc* (darker) and *lumen* (lighter) (Table 1). In addition to the specific colours of the face, there are other particular terms such as *prasinus*, which in Greek literally translates as '*leek green*', whose tone is similar to a mixture of green and black and was recommended for use in wall painting as an alternative to *viridi*, plain green.

We are studying one of the masterpieces of European Romanesque art (UNESCO World Heritage Site 2000), the mural painting in the central apse of the church of Sant Climent de Taüll, consecrated in 1123[1] and dating from the early 12th century (Vall de Boí, Alta Ribagorça, Catalonia) [13]. The quality of the paintings became internationally known in a 1911 article published in the The Burglinton Magazine [14,15], which praised the brush strokes, shapes and colours. Between 1919 and 1921, the paintings were detached from the original location, as part of a campaign led by the Junta de Museus de Catalunya to prevent them from being plundered from isolated Pyrenean churches and, transferred to a new support using a calcium caseinate adhesive. They are currently conserved and exhibited in the Museu Nacional d'Art de Catalunya (Fig. 1). Most of the studies on this pictorial set have a historiographical or iconographic approach [16–24] and, only a few focus on the chemical composition of the materials [25–27], which include blue pigment aerinite, yellow ochre, red haematite and cinnabar, and carbon black [25].

2. Research aim

In order to assess the extent to which Pyrenean Romanesque painters were aware of and applied the directions given in the treatises, and given the proliferation of instructions on the depiction of the face of the figures, our study focuses in this icono-

[1] In one of the painted columns of the nave is the text: ANNO AB INCARNACIONE DNI: M: C: XX: III: III: IDUS: DBR VENIT RAIMVNDUS EPC BARBASTRE NSIS CONSECRAVIT HAC ECLESIA IN HONORE SANCTI CLEMENTIS MARTIRIS ET PONENS RELIQUIAS IN ALTARE SANCTI CORNELLI EPISCOPI ET MARTIRIS.

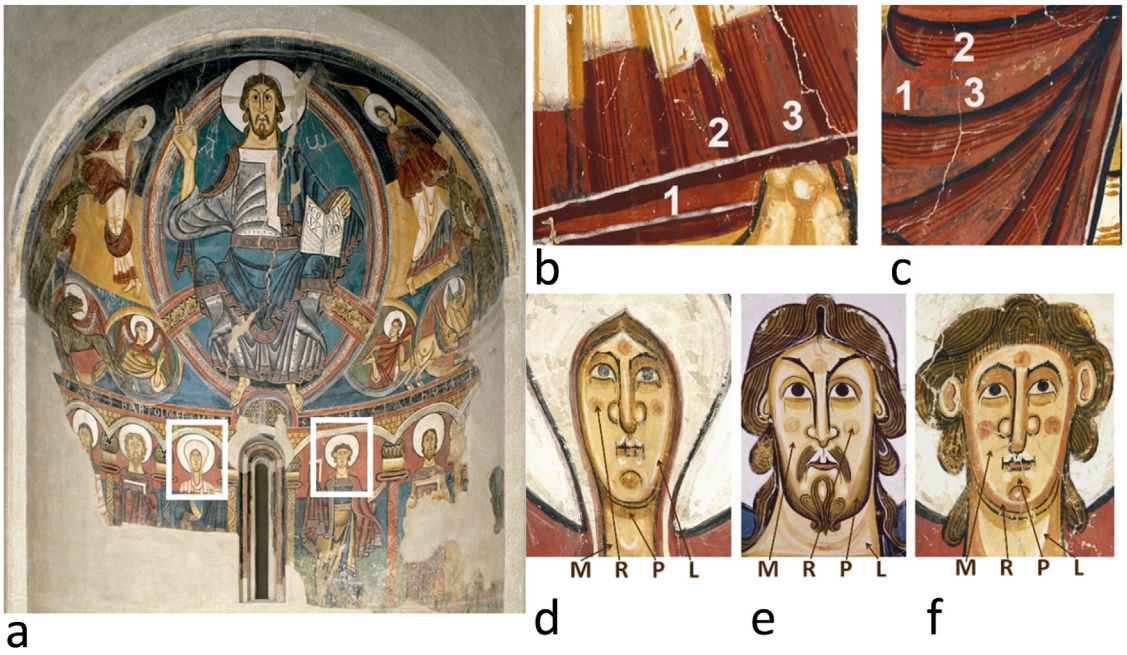


Fig. 1. a) Mural paintings of the central apse of Sant Climent de Taüll preserved in the Museu Nacional d'Art de Catalunya. b) and c) The three-tone system can be seen in some details of the red polychromies and in the faces of d) the Virgin Mary, e) the *Maiestas Domini* and f) Saint John. 1: mid-tone, 2: darker tone, 3: lighter tone for the red polychromies and, M (*membrana*): mid-tone, R (*rosa*) and P (*posc*): darker tones and L (*lumen*): lighter tone, for *carnation*. (© Museu Nacional d'Art de Catalunya. Barcelona 2023).

Table 2
List of analysed samples of the mural paintings in the central apse of Sant Climent de Taüll.

	COLOUR/TONE	DESCRIPCTION OF POLYCHROMIES	SAMPLE	ORIGIN
CARNATIONS	*Membrana* (M)	carnation	**R-00-M2**	Hand of Sant Peter
	Rosa (R)	pinkish	**R-13–21**	Shadow line of the neck of Saint John
	Posc (P)	dun shadow over carnation	**R-16–5**	Dark paint stroke around the face of the Virgin Mary
	Lumen (L)	white over carnation	**R-16–3A**	Light paint stroke on the face of the Virgin Mary
		white over black contour line	**R-16–6**	Light paint stroke on a face
HAIR	Brown/dun	black over hair	**R-13–29**	Contour line on the hair of Saint Bartholomew
		hair	**R-13–22**	Hair of Saint John
OTHER		dun	**R-13–33**	Dark paint stroke of a decorative element on the side of the figure of the Virgin Mary
	Yellow ochre	yellow ochre over white	**R-98–2a**	Ochre decoration of the dress of a cherub
	White	white	**R-13–32–1**	Nimbus of the Virgin Mary
		white	**R-13–32–2**	Nimbus of the Virgin Mary
RED POLYCHROMY	Red	altered colour over a red ochre	**V-13–28**	Decorative line of the book of Saint John
		altered colour over dark red	**V-13–38**	Decorative line of the dress of Saint John
		altered colour over a red ochre	**V-13–26**	Dark decorative line of the dress of a Saint
		altered colour over a red ochre	**V-13–16**	Decorative dark line of the dress of Christ in Majesty
		dark red over white	**V-13–14**	Decorative *mandorla* border

graphic element. We will also study the use of the three-tone system widely described in the treatises for other red coloured elements of the paintings, particularly, in the clothing.

3. Material and methods

A selection of representative samples of different carnation colours and red polychromies were studied, together with hair brown and other related colours (white, yellow ochre and brown or dun), which help contextualize the results (Table 2).

All samples exhibit a complex submillimetric layered structure, consisting of a combination of original materials and transformation products caused by weathering and ageing. Their study requires obtaining thin cross sections of the paint samples (Fig. 2) and analysing them using instrumental techniques with sufficient spatial resolution to determine individual components (typical particle sizes $<$ 1 μm to 50 μm) in each of the strata [28–30]. A combination of microanalytical techniques, micro-infrared spectroscopy (μ-FTIR), synchrotron-based micro-x-ray diffraction (μSR-XRD), scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS), and Optical microscopy (OM), was used to obtain precise information on the composition and distribution of the compounds in the sequence of micrometric layers.

Optical images were obtained with a Reichert-Jung POLYVAR MET Optical Microscope and, μSR-XRD was performed at XALOC beamline at the Alba synchrotron (Cerdanyola del Vallès, Barcelona) [31] the low energy $<$15 keV, high brilliance and focused beam 50 $\times$ 7 μm^2 (width $\times$ height FWHM) together with the noise-free large-area photon counting detector (Pilatus 6 M) allowed the identification of the crystalline compounds present in the painting layers. (For further details see Supplementary Information)

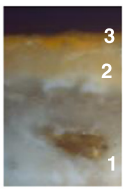
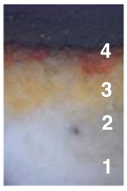
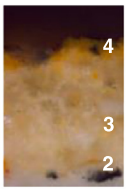
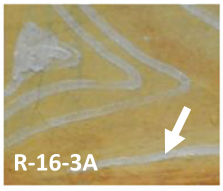
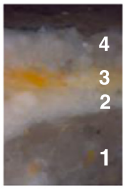
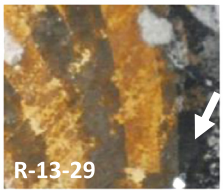
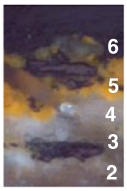
	SAMPLE LOCATION	OM IMAGES	LAYER DESCRIPTION	COMPOSITION
M mid-tone CARNATION			**3 mid-tone** 10-20 μm	FeO(OH) goethite, $CaSO_4 \cdot 2H_2O$ gypsum, silicates, $CaC_2O_4 \cdot nH_2O$, $CaCO_3$ calcite
			2 mid-tone 30-40 μm	FeO(OH) goethite, $CaSO_4 \cdot 2H_2O$ gypsum, silicates, $CaCO_3$ calcite
			1 mortar > 1200 μm	silicates, $CaCO_3$ calcite
R dark shade CARNATION (pink)			**4 pink** 15-25 μm	HgS cinnabar, $PbCO_3$ cerussite, FeO(OH) goethite, silicates, $CaSO_4 \cdot 2H_2O$ / $CaSO_4$, $CaC_2O_4 \cdot nH_2O$, $CaCO_3$ calcite
			3 mid-tone 60-90 μm	FeO(OH) goethite, $CaSO_4 \cdot 2H_2O$ gypsum, silicates, $CaC_2O_4 \cdot nH_2O$, $CaCO_3$ calcite
P dark shade CARNATION (brown)			**4 brown** 15-25 μm	FeO(OH) goethite, HgS cinnabar, carbon, $CaSO_4 \cdot 2H_2O$, silicates, $CaC_2O_4 \cdot nH_2O$, $CaCO_3$ calcite
			3 mid-tone 50-80 μm	FeO(OH) goethite, $CaSO_4 \cdot 2H_2O$ gypsum, silicates, $CaCO_3$ calcite
			2 drawing line 3-5 μm	FeO(OH) goethite, carbon, kaolinite, muscovite-illite, $CaC_2O_4 \cdot nH_2O$, $CaCO_3$ calcite
			1 mortar	silicates, $CaCO_3$ calcite
L light CARNATION (over black line)			**5 white** 15-20 μm	>>$CaSO_4 \cdot 2H_2O$ gypsum, $CaC_2O_4 \cdot nH_2O$, $CaCO_3$ calcite
			4 black 25-30 μm	$CaC_2O_4 \cdot nH_2O$, carbon, $CaCO_3$ calcite
			3 mid-tone 50-80 μm	FeO(OH) goethite, $CaSO_4 \cdot 2H_2O$ gypsum, silicates, $CaCO_3$ calcite
			1 mortar	silicates, $CaCO_3$ calcite
L light CARNATION			**4 white** 15-30 μm	>>$CaSO_4 \cdot 2H_2O$ gypsum $CaC_2O_4 \cdot nH_2O$, $CaCO_3$ calcite
			3 mid-tone 10-15 μm	FeO(OH) goethite, Fe_2O_3 hematite, $CaSO_4 \cdot 2H_2O$ gypsum, silicates, $CaCO_3$ calcite
			2 mortar	silicates, $CaCO_3$ calcite
BROWN HAIR POLYCHROMY			**6 black** 7-20 μm	$CaC_2O_4 \cdot nH_2O$, carbon, $CaCO_3$ calcite
			5 brown hair 30-50 μm	FeO(OH) goethite, carbon, Fe_2O_3 hematite, $CaCO_3$ calcite
			4 white nimbus - 7-20μm	$CaSO_4 \cdot 2H_2O$ gypsum, $CaSO_4$ anhydrite, $CaCO_3$, calcite
			3 drawing line 5-8 μm	FeO(OH) goethite, carbon, kaolinite, muscovite-illite, $CaC_2O_4 \cdot nH_2O$, $CaCO_3$ calcite
			2 mortar	silicates, $CaCO_3$ calcite
			1 casein mortar (cheese and lime)	$CaCO_3$ (calcite and vaterite) , $Ca(OH)_2$,portlandite, $Mg(OH)_2$ brucite, carboxylates, phosphates, protein

Fig. 2. Location of the samples, optical images of the cross-sections of the samples and composition of the paint layers of the faces (M, R, P and L of carnation and hair) of the Sant Climent de Taüll wall paintings (table 2). All compounds have been identified by μFTIR and SR-µXRD except phosphates, protein and carboxylates which have been identified only by μFTIR and cinnabar, carbon and haematite only by SR-µXRD. The elemental chemical composition has been verified using SEM-EDS.

4. Results and discusion

After a visual inspection, the faces of Sant Climent de Taüll paintings show the presence of a yellow ochre base colour (M), a pink (R) and brown or dun (P) colour to draw and outline the different face elements, white brush strokes (L) applied in strategic areas, a brown colour for the hair and black for the contour lines (Fig. 1).

Sant Climent paintings consist of a superposition of layers, mixtures of pigments the composition and chromatism of which is described in the following sections (Fig. 2), starting with *lumen* (L), a white pigment that was added to all other carnation colours.

4.1. White layers (L, light in carnations and nimbuses)

Calcium sulfate (namely gypsum, $CaSO_4{\cdot}2H_2O$, and anhydrite, $CaSO_4$) is present in both the light effects in the carnations (L) and in the white nimbuses of Sant Climent's paintings samples (Fig. S1). Calcite, $CaCO_3$, probably from the mortar layer below or from the binder is also present. The proportion of gypsum/anhydrite versus calcium carbonate is higher in the nimbuses than in the light brush strokes on the carnations, as the relative intensity of infrared bands (Fig. S1a) indicates and also in the diffraction patterns (Fig. 3).

These white layers include a few small Sr containing particles and identified by SEM-EDS (Fig. S1e) and μSR-XRD as a crystalline strontium sulfate, $SrSO_4$ (celestine). Celestine traces in gypsum are related to the materials source [32–34] (Fig. 3, S2).

In fact, the Montpellier Manuscript mentions the use of gypsum as white pigment, but only to be applied on "*dry walls*" [6]. Usually, only calcite is detected in white coloured areas, although dolomite, is also found in Roman mural paintings [35]. The calcium sulphate/carbonate combination is indeed unusual, which nevertheless has been identified in other Vall de Boí mural painting sets as well [36]. In fact, greater luminosity and opacity are obtained due to the light scattering of large crystals of gypsum and anhydrite. Although being different in composition, the effect created by this white pigment mixture is similar to that of the *bianco sangiovanni* [9] described by Cennini, grinding $Ca(OH)_2$, immersing it in water for several days and letting it sundry. This process results in a mixture of $CaCO_3$ with about 30% $Ca(OH)_2$ [37]. The presence of crystalline calcium carbonate particles produces a lighter, more covering white, compared to the more translucent layer obtained by the carbonation of $Ca(OH)_2$ [37].

Thin white brushstrokes (L) are applied over the base colour (M) or even over the black contour lines (Fig. 2). Similarly, as recommended by the medieval treatises, they were applied just at the end of the pictorial process in other Romanesque mural paintings [38]. Like the recipes for carnations compiled in *Hermeneia*, L is *purely* white, i.e. not mixed with *membrana* in Sant Climent paintings. This contradicts Teophilus' instructions, which recommend lightening the mid-tone (M) with white for the lighter areas.

4.2. Yellow ochre base colour layer (M, mid-tone carnations)

The compounds associated with the yellow ochre pigment were identified by µSR-XRD: iron (III) oxide and hydroxide, goethite (FeO(OH)), muscovite-illite-like phyllosilicates, rutile (TiO_2) and quartz, (SiO_2) (Fig. S2). In addition, some of the base colour/mid-tone layers include traces of red Fe-containing particles (identified by SEM-EDS, Fig. S2 d-g), which could be related to iron (III) oxide (haematite, Fe_2O_3).

The presence of calcium sulphate ($CaSO_4{\cdot}2H_2O$) together with calcite and traces of celestine (Fig. S2) indicates the mixing of white pigment with ochre to obtain the mid-tone (M). Not only the composition but also the colour saturation of carnations is thus different from that of other ochre paints.

The resulting mid-tone M resembles the *membrana* descriptions in Teophilus and *Hermeneia*, which unlike the *membrana* in the Montpellier manuscript, do not contain green. The base colour layers are applied directly on the mortar and are thinner in the peripheral areas close to the contour lines; in fact, this was explicitly recommended in the *Hermeneia*.

4.3. Pink layer (R, dark shade in carnations)

Pink layers (R) contain all the compounds present in the base colour (M) plus cerussite ($PbCO_3$,) and cinnabar (HgS). Cinnabar, alone or, frequently, mixed with minium (Pb_3O_4), gives a red colour to the layer. Here, minium containing some impurities such as PbO, reacted with carbonate and hydrogen carbonate ions (CO_3^{2-}/HCO_3^-), from atmospheric CO_2 dissolved in the wet lime, producing cerussite as a reaction product [37,39-41]. The composition of this pink layer, applied over the mid tone (M) (Fig. 4), mirrors Teophilus' description of the *rosa* colour "*Then mix with the plain flesh colour a little vermilion and a little red lead and prepare the colour which is called rose*"[2] [4]

4.4. Brown or dun layer (P, dark shade in carnations)

Dun coloured layers contain the same compounds present in the base colour (M) mixed with black particles which show a graphite microstructure, and small amounts of cinnabar (Table 2, Fig. 2 and S3). The dark shade and colouring strength of carbon depends on the size of the particles and agglomerates of particles [42,43]. Whereas small particles produce a brown-red shade, larger particles lead to a blue shade. The dun colour (P) appears greenish in Sant Climent de Taüll paints.

In fact, the *posc* colour described in the treatises might be associated to the dun colour applied over the carnation mid tone layer. Nevertheless, *posc* is described to contain *prasinus*, the nature of which according to the scholars is uncertain, so the composition of *posc* is not yet clear.

4.5. Prasinus *and* posc

Unfortunately, to date there has been no consensus amongst historians and translators as to the composition of *prasinus*. It has been suggested to be either an organic dye, a green earth (i.e. celadonite or glauconite [4,44] or a green chalcedony (a type of quartz) [5]. Teophilus cites this colour when specifying how shadows are to be outlined using the *posc* colour:"*When you have mixed the flesh-colour pigment and have laid in the faces and nude bodies with it, mix with it prasinus, the red that is burnt from ochre, and a little cinnabar, and so make shadow pigment.*"[3] according to the translation of Hawthorne and Stanley [5]. Definitions of *prasinus* are given within the same text and also in the Montpellier manuscript. In Teophilus text it is described as: *"a pigment, which looks like viridian mixed with black. Its nature is such that is not ground upon stone, but, when put in water, it dissolves and is then carefully strained through a cloth. On a new wall it can be very usefully employed as a green colour*" ,[4] according to the translation of Dodwell [4]

[2] *Deinde misce cum simplici membrana modicum cenobrii et parum minii, et confice colorem qui dicitur rosa* [4].

[3] *Cum uero membranam miscueris et inde facies et nuda corpora impleueris, admisce ei prasinium et rubeum, qui comburitur ex ogra, et modicum cenobrii, et confice posc* [4, p. 5-7].

[4] *Qui prasinus est quasi confectio quaedam habens similitudinem viridis coloris et nigri, cuius natura talis est, quod non teritur super lapidem sed missus in aquam res-*

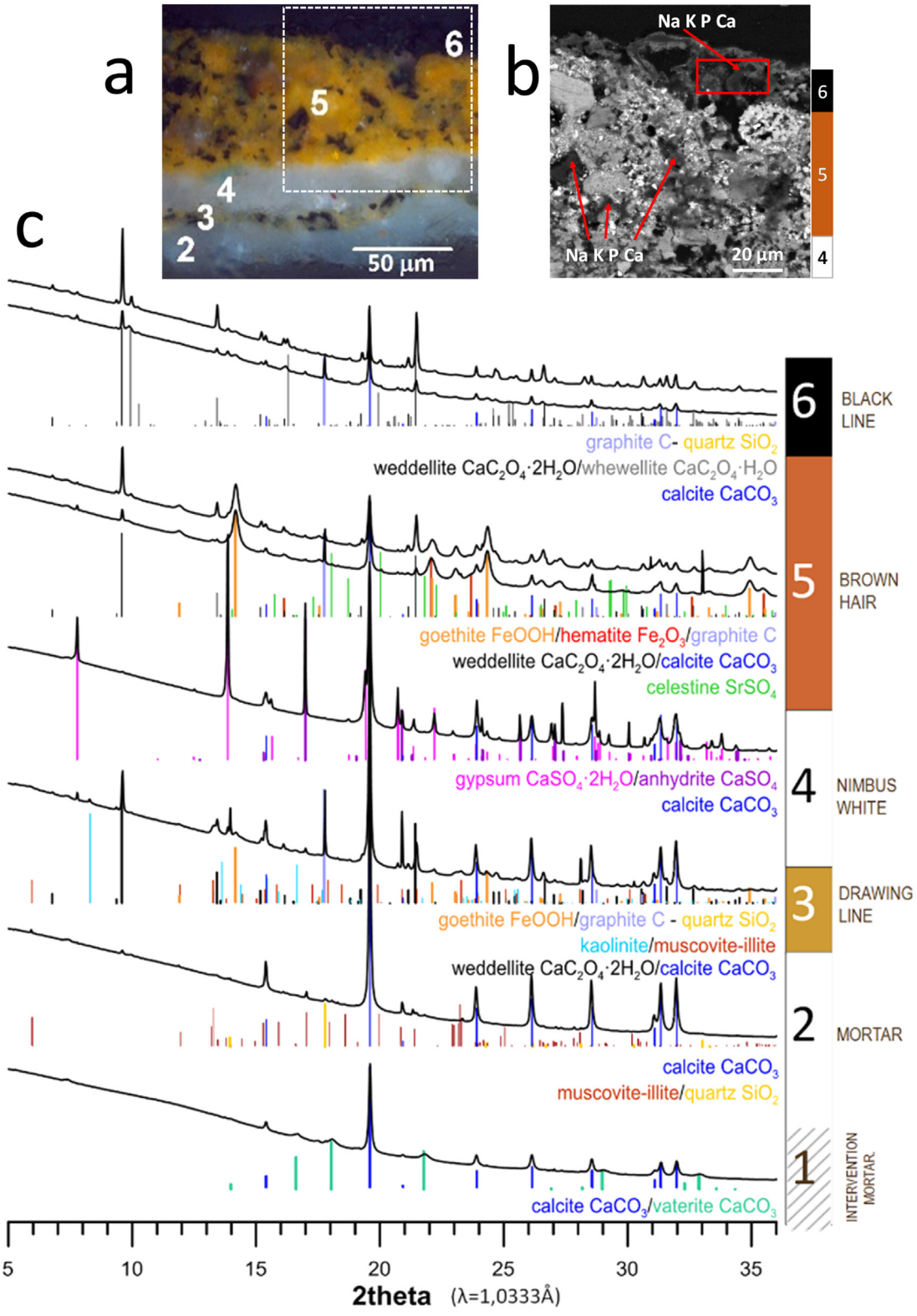


Fig. 3. a) Optical microscopy image of a cross-section of R-13–29 taken from the hair of Saint Bartholomew from the central apse from Saint Climent de Taüll mural paintings. 2: mortar, 3: drawing line, 4: white of the nimbus, 5: hair and 6: black line. b) Backscattered electron image corresponding to the square in optical image, indicating the minor elements present in the carbon particles and c) µSR-XRD patterns taken from the different layers.

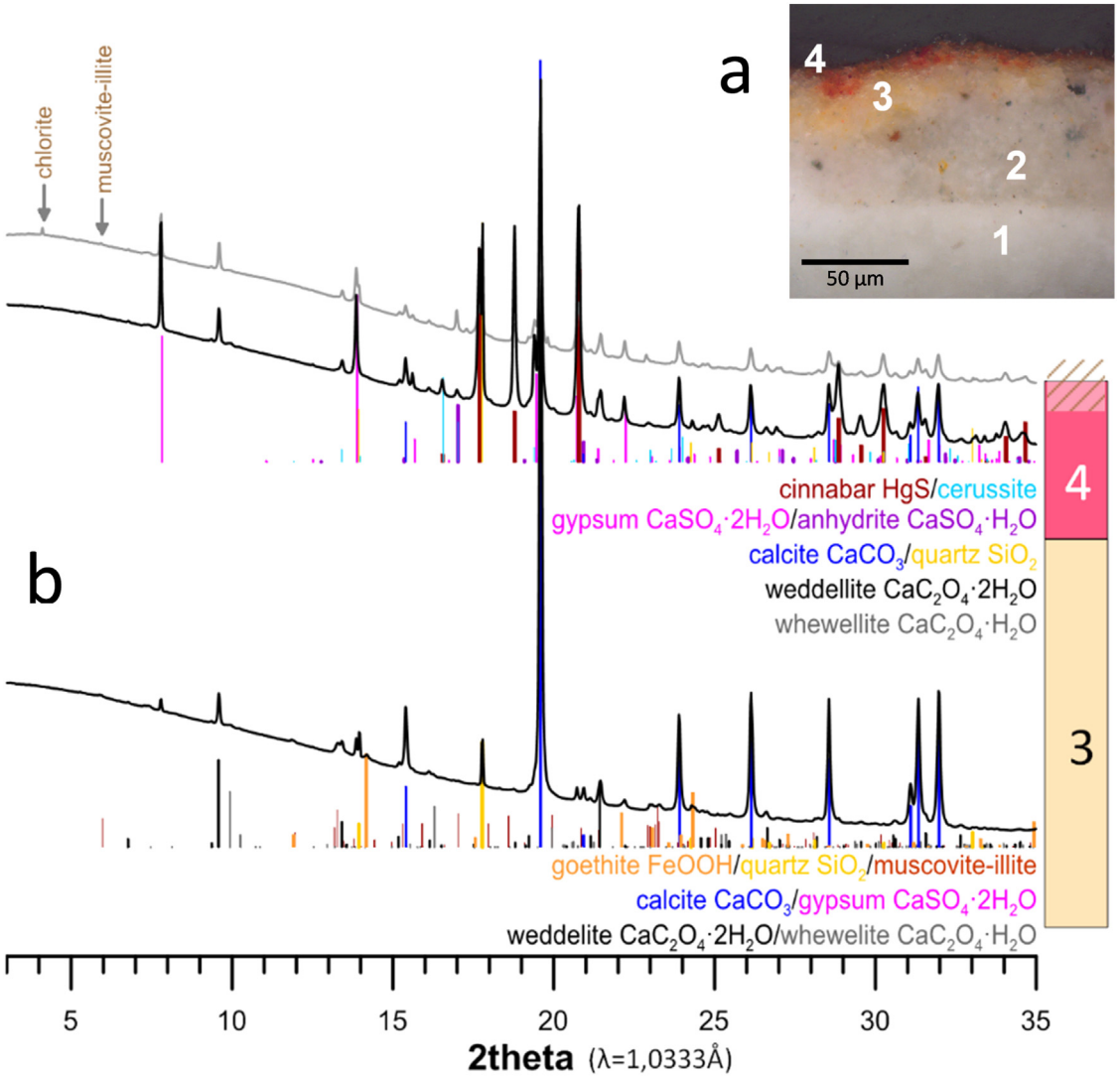


Fig. 4. a) Optical microscopy image of a section of R-13–21 of Sant John from the central apses from Sant Climent de Taüll mural paintings. 1: intervention mortar, 2: mortar, 3: *membrana* (mid-tone) and 4: *rosa* (dark shade). b) µSR-XRD patterns taken from the different layers.

The chromatism described for *prasinus* in medieval treatises is similar to the greenish colour obtained by mixing yellow ochre and carbon black. In fact, combining black and yellow to obtain green was a recurrent practice in this historical period. For instance, according to *Mappae Clavicula* black must be mixed with orpiment to obtain *gladus* green [45]. Therefore, we could hypothesize that *prasinus* is a mixture of yellow ochre and black, and the final dun colour (P) was obtained by adding *prasinus*, red ochre and a small amount of cinnabar to *membrana* (yellow ochre + white) (Fig. 2 and Fig. S3). Only in this case, the composition of the dun colour would match the Teophilus' description of *posc*, whose use and colour is very similar to the typical byzantine *Panselinos colour*, described in *Hermeneia*.

4.6. Brown (hair polychromy)

The brown of hair consists of a mixture of heterogeneous particles of goethite and haematite (1 to 50 µm) with carbon black (low amounts of Na, K, Mg and P, identified by SEM-EDS, denoting its vegetable origin), calcium carbonate, and, occasionally, celestine (Fig. 2, 3 -layer 5). It contains a lower proportion of phyllosilicates compared to the base yellow ochre (M) and dun (P) colours. This fact suggests the use of two different yellow ochres, one for the carnations (Fig. 4 -layer 3, Fig. S2) and another for the hair (Fig. 3 -layer 5). The existence of two different ochres seems to be a common medieval pictorial practice, already mentioned in Cennini's text (LXVII chapter): "*Take as much as a bean of dark ochre (for there are two kinds of ochre; light and dark)*" [8,9].

The green colour obtained by mixing yellow ochre and black switches to brown when haematite particles are added. This mixture corresponds to one of the recipes from the "Mixtures and modelling" part of the Montpellier manuscript and was used to paint the hair of young characters: *ochre, red and black are mixed, and the hair of youths is filled in*[5] [6 p124].

4.7. Red (clothing and other red polychromies)

The three-tone system is also present in the clothing and other red polychromies of Sant Climent (Fig. 1). The mid-tone is made of phyllosilicates (kaolinite) with small (<1 µm) iron (III) oxide

oluitur et per pannum diligenter colatur; cuius usus in recenti muro pro viridi colore satis utilis habetur [4, p.5].

[5] *Misceatur ocrea rubeum et nigrum et ompleantur capilli iuvenum*[4, *p.* 267].

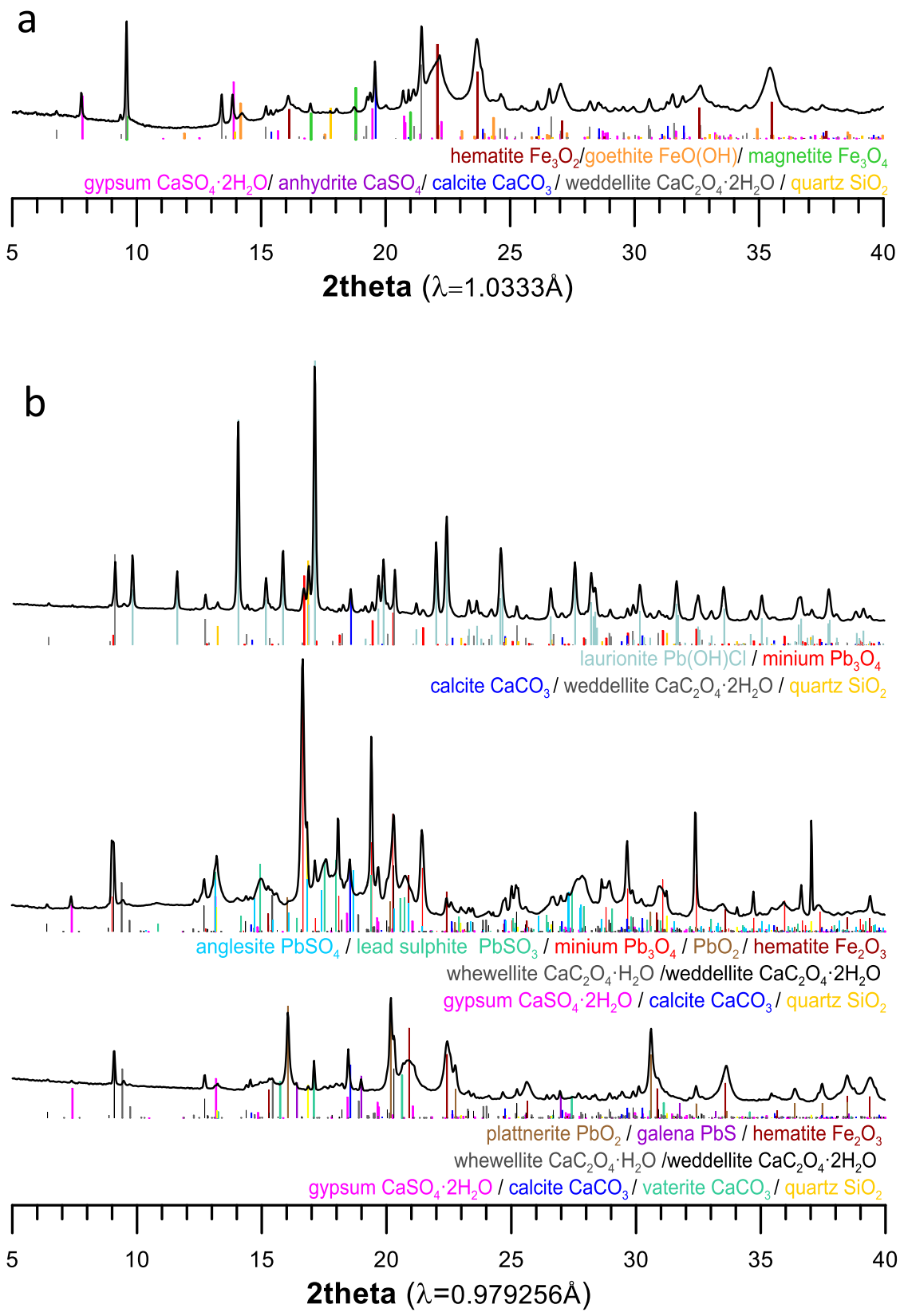


Fig. 5. µSR-XRD patterns taken from the surface layers of red polychromies from Sant Climent de Taüll mural paintings (table 2). a) dark red decorative border from the *mandorla*, (V-13–14) and, b) altered light colour of the decorative lines of a book, V-13–28 (top) and of the dresses, V-13–26 (middle), V-13–16 (bottom).

(haematite) particles and quartz. It was extensively applied and appears mostly in the inner/base layers as wide strips delineating the contour of the *mandorla* (the oval frame or halo, with the shape of an almond, which surrounds the *Maiestas Domini*). Darker red colour contains mainly large (> 1 μm) haematite particles [46], with few magnetite (Fe_3O_4) and goethite particles (Fig. 5a). This colour was also used to outline shadows on clothing and to paint details and elements of iconographic relevance.

Thick strokes of light applied delineating little decorative elements and minute details were originally red, composed of minium and, occasionally, also cinnabar. This composition is consistent with the recommendations given by Teophilus. However, as they are collected in the XIVth chapter: *Mixing colours for draperies on a panelled ceiling,* they are not exclusive for mural paintings [4]. However, μSR-XRD shows that the surface layers contain also secondary lead reaction products: white compounds like lead hydroxychloride (laurionite, Pb(OH)Cl), lead sulphate (anglesite, $PbSO_4$) and lead sulphite ($PbSO_3$) and dark compounds like lead sulphide (galena, PbS) and lead oxide (plattnerite, PbO_2) (Fig. 5b). Different proportions of the white and dark lead species give rise to a chromatic variability in the fine surface brushstrokes. Plattnerite and laurionite were also identified in thin brushstrokes containing minium and cinnabar from the Romanesque mural paintings of Saint-Pierre d'Orjout à Bordes-Uchentein (Ariège), where an organic binder was mixed with the pigment [47]. This suggests the use of the same technique and pictorial style in an area relatively close geographically to Sant Climent de Taüll. In the Taüll case, the original organic matter cannot be distinguished. The complex process of detachment and reattachment of the painting included, amongst other steps, the application of cotton canvas impregnated with a strong animal skin glue (a gelatinous substance obtained by boiling animal connective tissue), from which, despite being removed in subsequent steps, residues remained. However, the distinction between *fresco* for the inner layers and *secco* for the finishing brushstrokes can still be recognized by observation of the carbonation microstructure in SEM images and calcium EDS distribution maps [48,49], shown in Figure S4.

Also, the presence of weddellite ($CaC_2O_4{\cdot}2H_2O$) and whewellite ($CaC_2O_4{\cdot}H_2O$) were determined by μSR-XRD (Fig. 3-5, S2) and by μ-FTIR (Fig. S1, S3). The presence of calcium oxalates may be related to the use of an organic binder in the pictorial layers applied al *secco* [50–52], but also the use of organic substances to dye inorganic pigments, also described in some medieval manuscripts [6], to a biological origin [53] or, as already commented, to the degradation of the proteins used in the detachment and transfer of the paintings.

4.8. Drawing lines

The detachment of the paintings exposed the original drawing lines in the Sant Climent de Taüll wall (Fig. S5). These lines applied with a brush helped to delineate the pictorial composition before the application of the colour. They have lighter or darker (nearly black) greenish colours and are composed of carbon black, goethite, quartz and silicates (Fig. 3b), similarly to the dark shade carnation (P). On the contrary, the drawing lines present in other Romanesque mural paintings are red [38,54]. In the apse of Sant Climent, some red marks were also made by hitting the wall with a vibrating rope to delimitate the drawing areas.

The dark green colour made of a black and yellow ochre mixture used for the drawing lines is called *verdaccio* by Cennini (*Il libro dell'Arte,* LXVII and LXXXV chapters) [8].

The drawing described in the *Hermeneia* also combines black and yellow ochre, but in this case, they are applied sequentially: a sketch was painted with diluted yellow ochre over which the final drawing lines were applied with carbon black.

On this basis, we propose that the mixture of yellow ochre and black identified for the dun colour (P) and which we associate with the *prasinus* could be the precedent of *verdaccio*. They have the same chromatism and uses (drawing lines and facial shades).

5. Conclusions

Analysis of the Sant Climent de Taüll paintings has enabled us to verify a series of pictorial indications and recommendations contained in various medieval treatises. In particular, the use of the three-tone procedure (chromatic triplet) to model (create volumes and shadows) both faces and clothing. Four basic colours were used: white, black, yellow and red. Nevertheless, up to eight different pigments are carefully mixed according the published recipes, to obtain a variety of tones. These findings challenge two widely accepted ideas about medieval painting, in particular Romanesque painting, namely: 1) the palette of Romanesque wall paintings was limited and 2) the materials were not mixed in order to preserve their purity.

In fact, and despite the lack of analytical studies, the application of the three-tone procedure for the representation of faces is widespread amongst Pyrenean and Pre-Pyrenean Romanesque mural painting sets, which suggests a systematization in the *modus operandi* transmitted during the training period of medieval painters. In view of the pictorial process applied at Sant Climent, the training and knowledge of the masters seem to merge the Byzantine tradition, gathered in *Hermeneia*, with the western tradition recorded in *De Diversis Artibus* by Teophilus.

Moreover, we have observed that mural painters follow the instructions initially conceived for other supports or artistic techniques. Consequently, the same style is found in other pictorial contexts. For instance, the three-tone procedure (which includes *membrana* as mid-tone, *rosa* and *posc* for the darker tones and *lumen* for the lighter tones) is also present in the faces of the figures in the Catalan Romanesque wooden antependium.

Finally, although it was not our main objective, our study has also shed light to the question of the use of *secco* or *fresco*, which was not clearly indicated in the instructions of the manuscripts. The three-tone procedure generates a superimposition of two or three layers, also in the mural paintings. The inner layers, painted right on the still wet lime mortar, show the typical carbonation microstructure of *fresco*, while the surface layers for the outline of geometric decorative elements and figures, which required longer working times, were applied al *secco*, mixing the pigments with either an organic medium or with diluted lime, depending on their compatibility with each colour.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2023.05.021.

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