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Multi-analytical characterisation of blotting sands on documents from religious orders in Portugal (16th-19th centuries)

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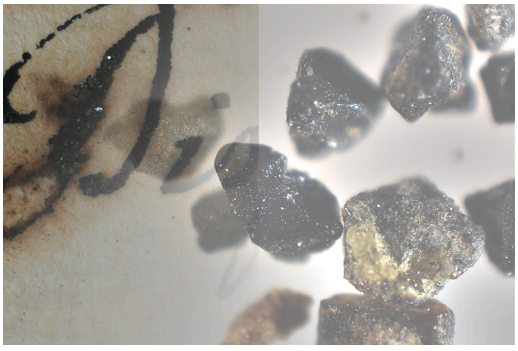
HIGHLIGHTS

- Uncover the blotting sands from the account books of Portuguese religious houses.
- SEM-EDS and vibrational spectroscopy revealed samples dominated by Fe-Ti oxides.
- There was a Portuguese preference for black sands irrespective of region.
- Sands were probably collected locally and no centralised acquisition was found.

GRAPHICAL ABSTRACT



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ABSTRACT

Too little is known about *areia de escrever*, i.e., blotting sands, the intriguing particles sprinkled on freshly written scripts to accelerate the drying time of the ink. Blotting sands constitute a valuable but underestimated historical source.

This work investigated the blotting sands used on the account books of the religious houses scattered across continental Portugal and Madeira Island (16th-19th centuries). The sands were mainly composed of different minerals, predominately black sands, but in a few cases, minerals were found mixed with gums, paper cocoons or bone shavings. The combined use of SEM-EDS, μ-Raman and FT-IR techniques uncovered the materials' chemical or mineralogical composition and morphology. This approach, allied with image analysis and statistics complemented with multivariate analysis, allowed us to look for trends between the samples and hypothesise about their provenance. Heavy minerals, such as ilmenite, hematite and almandine, were identified as major

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components, together with other silicates (e.g. quartz). Samples were dominated by medium-sized grains with shape features indicating texturally mature sediments resulting from a medium-to-long sedimentary transport. Due to shorter geological transport distances, Madeira Island was the exception, with more angular grains. This work allowed us to uncover blotting sands, value them as historical sources, and establish a roadmap for their use in Portugal, aiming to pave the way towards a more global context in Europe.

1. Introduction

1.1. An overlook on blotting sands

From the 11th century onwards, the handwriting process in Europe experienced an adjustment with the emergence of new materials and techniques: paper gradually replaced parchment, and the indelible iron-gall inks supplanted carbon inks [1]. At the same time, various *instrumenta scriptorii* [2], such as inkwells, quill pens, curved knives, and blotting materials, like blotting paper and sand kept in adorned sanders, began to decorate desks [3–5]. Writing quills were usually made from swan or goose feathers and cut with special knives [4,5]. Carefully prepared inks were poured into the inkwells made of lead, ceramic or other materials, where the quills were rhythmically dipped into while writing [3]. Blotting paper was then used to absorb the excess ink, while blotting sands were intended to accelerate the drying time. Many of these writing accessories were illustrated in Byzantine and Greek miniatures [6] and described in various treatises [7,8].

Areia de escrever, arena scriptoria or blotting sands are small particles sprinkled evenly on freshly written scripts [9,10]. While a substantial volume of recipes for inks can be found in old literature, little information exists on blotting sands. However, it is often included in European books where handwriting instruments are described [11,12].

Many religious orders were crucial in Portugal from the 12th century onwards, especially considering culture and literacy. The wealthiest families from different social groups always had a son or a daughter in a convent or monastery, living a religious life. Unlike most of the population, many nuns/sisters and friars/monks learned to read and write fluently, achieving substantial cultural literacy.

The number of members of the religious orders – when referring to "religious orders", we meant religious communities differentiated by their canonic profiles according to the Code of Canon Law – increased after the Counter-Reformation (1545–1563) until the mid-18th century. In 1652, around 449 religious houses existed in the country [13], and in 1763 the number increased to 601. This last number includes the Jesuit houses, whose members were expelled from Portugal in 1759 [14].

All these houses had account books for their daily life management, where the purchase of the goods was registered, with detailed information on the individual items, including prices and quantities. The analysis of the recorded expenditure can show when a religious house purchased ink, pens, paper and sand. From the quantities, specifications and context, it is possible to distinguish between sand for building works and handwriting drying [15]. From the available historical research, these books on the purchase and use of sand for handwriting - dating from the 16th century onwards - are among the most comprehensive Portuguese sources inherited by us.

Furthermore, few works were published on the analytical characterisation of blotting sands [9,16,17]. Interestingly, what is known is that the sands could be of various natures: mineral (e.g. mica, quartz, and iron oxides), organic (e.g. gums, wood, and bone shavings) and artificial (e.g. tarnished metals and stained glass). Minerals seemed to be the top preference, and the metallic lustre presented by many sulfide or oxide minerals must have intervened in the choice since it would give a shiny appearance to the writings [9].

Several questions about blotting sands remain unanswered: are the materials used in Portugal similar to those found in other parts of Europe? Where and how were they obtained?

Here, we present a systematic study of the blotting sands from the different religious houses/communities scattered around the country. Combined SEM-EDS, μ-Raman, and FT-IR spectroscopies allied with statistics and multivariate analysis allowed us to map the materials used in Portugal from the 16th to the 19th centuries. Besides, we intended to understand if a particular taste dominated the materials' choice or if those in vogue were used. We could also contrast the results with those obtained in a previous work [17], where we scrutinised the blotting sands used by the Central Council of the Portuguese Inquisition, a central, dominant institution in the country, in the documentation sent to the Lisbon, Évora, and Coimbra Tribunals (16th-18th centuries).

This research was paramount to uncovering the use of blotting sands in Portugal and the historical source of information they constitute. Furthermore, we intended to draw attention to a topic of deep concern for those working on archival research and the conservation of written heritage who frequently collect substantial amounts of loose sands and ignore their value and the appropriate practices to protect them.

1.2. Religious institutions profile

The sampling of blotting sands was focused on the account books from 26 religious houses governed by distinct religious orders from continental Portugal and Madeira Island (Fig. 1). The religious houses were selected for the study considering their geographical location and the vast collection of surviving handwritten account books. Madeira was included due to its insular location and basaltic origin. Detailed information on the typology of the Portuguese convents, monasteries and religious houses studied can be found in the Supplementary Material (Table SM.1).

2. Material and methods

2.1. Sampling

Blotting sands were sampled from handwritten account books (16th-19th centuries) of Portuguese convents, monasteries and other religious houses from the North to the Alentejo regions, including Madeira Island (Fig. 1). Loosen blotting sands were collected by folium to Eppendorf tubes in a total of 185 samples. The careful sampling procedure enabled us to link each sample to a specific house and time period. A list of the analysed volumes and the context of the samples is detailed in Table 1.

2.2. Characterisation techniques and image analysis

2.2.1. Optical microscopy (OM)

A Leica M205 C stereomicroscope (©Leica Microsystems, Germany) was used to examine the grains' morphology and colour. Individual grain separation was carried out to define grain boundaries correctly using PELCO® Pro High Precision tweezers. High-resolution images (1024 × 1024 pixels or larger, 300 DPI) were acquired for image analysis (grain size and 2D-shape evaluation) using ImageJ® software.

2.2.2. Variable pressure scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (VP-SEM-EDS)

VP-SEM-EDS analyses were carried out in a variable pressure Hitachi™ S-3700 N SEM (Hitachi High-Tech® Europe GmbH, Germany) coupled with a Bruker™ XFlash 5010 SDD EDX® spectrometer (Massachusetts) with the detector resolution of 123 eV at the MnKα energy line. Esprit1.9® software was used for the EDS analysis. The samples

were deposited on a thin conductive carbon tape on aluminium sample holders. EDS analysis and imaging in the backscattered mode (BSE) were conducted with an accelerating voltage of 20 kV and 40 Pa in the chamber.

SEM-EDS study was carried out on a batch of 81 out of 185 samples. Samples with more than 50 grains were randomly divided into four similar fractions, with one exhaustively analysed for representativeness. Grain morphological evaluation based on SEM observation led to the division into the "angular" or "rounded" classes.

2.2.3. Micro-Raman spectroscopy (μ-Raman)

The Raman analyses were done on a HORIBA XPlora™ (Japan) spectrometer coupled with an Olympus microscope. A 50× objective (NA 0.75) was used to focus the 785 nm diode-type laser (125 mW, 1200 lines/mm grating) on the sample surface with a laser power of 1.1 mW. Spectra were recorded at 1 cm^{-1} in the 100 – 3000 cm^{-1} region with 10 to 25 accumulated scans and an exposure time of 5 to 25 s. Instrument calibration previous to the analyses was carried out with a Si standard (520.6 ± 0.1 cm^{-1}). The spectra were obtained at room temperature and processed using LabSpec software (HORIBA).

2.2.4. Micro-Fourier transform infrared spectroscopy (μ-FT-IR)

The organic materials were identified by μ-FT-IR on a Bruker Hyperion 3000® controlled by OPUS 7.2 software (Bruker™ Optics and Microanalysis GmbH, Germany) equipped with a Mercury-Cadmium-Telluride (MCT) detector. Both transmission and ATR modes were employed. A 15× objective and a compression microcell EXPress 1.6 mm, STJ-0169 (©S.T. Japan, Tokyo, Japan) were used in the former mode. ATR analyses were carried out with an 80 μm diameter germanium crystal and a 20x objective, in the range of 4000 to 600 cm^{-1} and a spectral resolution of 4 cm^{-1} and 64 accumulated scans for each analysis. Spectra interpretation were performed using the IRUG database and literature.

2.2.5. ImageJ® analysis performed on stereomicroscopic images

ImageJ® 1.51s software (LOCI, University of Wisconsin) was used to estimate the size and morphological properties of the blotting sands. Three parameters were selected and measured - Feret diameter (D_F), roundness (R) and circularity (C). The parameters definition and their corresponding formulas are available elsewhere [19].

Particle classification by size, based on the Feret diameter, was established according to Wentworth's grain size classification [20], divided into the following classes: "very coarse" (1.00–2.00 mm), "coarse" (0.500–1.00 mm), "medium" (0.250–0.500 mm), "fine" (0.125–0.250 mm), "very fine" (0.062–0.125 mm). Grains within the range defined for this scale are called "sands".

The main classes describing R include "very angular" ($0.12< R\leq 0.17$), "angular" ($0.17< R\leq 0.25$), "sub-angular" ($0.25< R\leq 0.35$), "sub-rounded" ($0.35< R\leq 0.49$), "rounded" ($0.49< R\leq 0.70$), and "well-rounded" ($0.70< R\leq 1.0$) [21]. C describes how close a grain is to the perfect circle shape (value of 1.0) with high circularity in the 0.70 to 1.0 range [22]. Sphericity measures how spherical a grain is (or circle, in 2D) [23,24] and is commonly used as circularity in the literature [24]. In this work, we used circularity values to discuss the grains' sphericity due to the high circularity of the grains under study.

The D_F, R, and C data of the grains within the 185 collected samples were used for the statistical studies.

2.2.6. Statistic and multivariate analysis

Grain size, morphology, and EDS chemical composition were described by statistical tools. Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) techniques were employed in

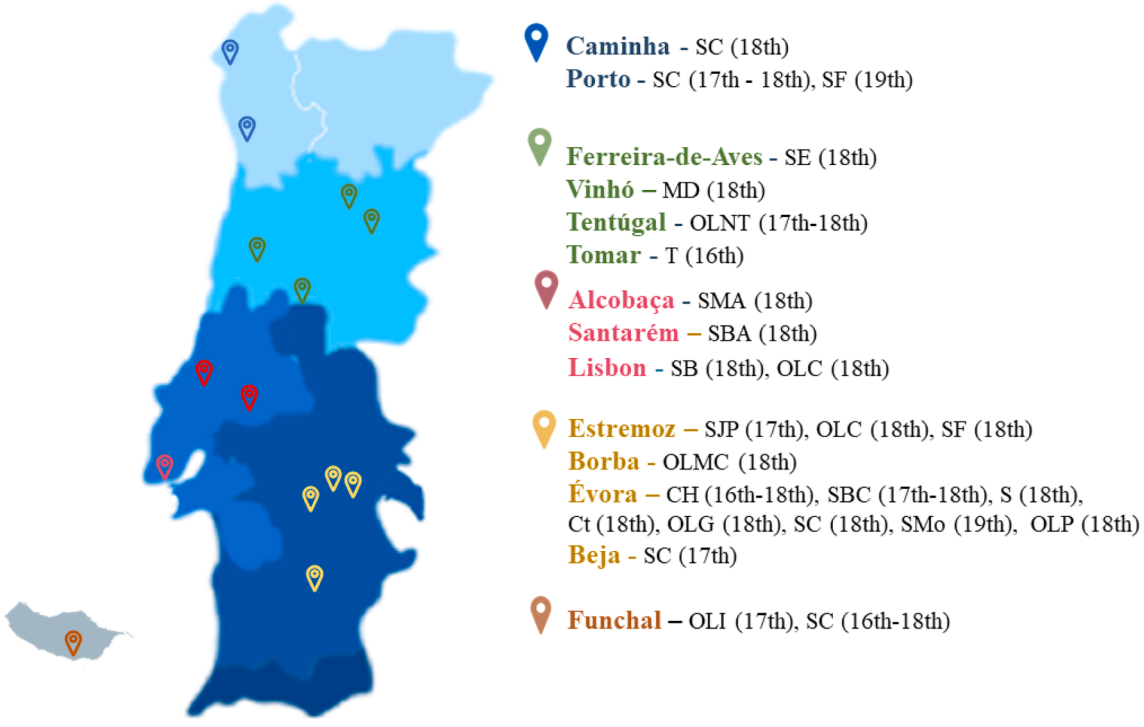

Fig. 1. Location of the Portuguese religious houses where the account books were written in mainland Portugal and Madeira Island. The regions are geographically defined according to the Portuguese territorial organisation in the period under study [18]. Ct - Convent of Cartuxa or Monastery of Santa Maria Scala Coeli; CH – Convent of Hawthorn; MD - Monastery of the Mother of God; OLC - Convent of Our Lady of Conception; OLI - Convent of Our Lady of Incarnation; OLG - Convent of Our Lady of Grace; OLMC - Convent of Our Lady of Light of Montes Claros; OLNT - Convent of Our Lady of the Nativity; OLP - Convent of Our Lady of Paradise; S - Convent of the Saviour of the World; SB - Convent of St. Benedict; SBA - Convent of St. Benedict of Apostles; SBC - Monastery of St. Benedict of Cástris; SC - Monastery of St. Clare; SE - Convent of St. Euphemia; SF - Convent of St. Francis; SJP - St. Convent of John of Penance; SMA - Monastery of St. Mary; SMo - Convent of St. Monica; T - Convent of Christ (Tomar).

multivariate analysis using these descriptors to address possible correlations between chemical and morphological composition and religious, geographical and date descriptions.

Python (version 3.9) programming language and Pandas [25], SciPy [26], Scikit [27], and Matplotlib [28] were used for data curation and for subsequent statistical and multivariate analysis.

The dataset for the samples' chemical description and multivariate analysis was based on the EDS results, according to which the minerals in the blotting sands were organised into eight groups, namely, Fe-Ti oxides (ilmenite), Fe oxides (hematite), silicates (e.g. almandine, quartz), Ti oxides (rutile, anatase), phosphates ((REE)-rich grains), carbonates, oxides (cassiterite), and sulfide (galena). The carbonate group was further divided into calcite and Ca-Mg-rich grains subgroups and the phosphate group was subdivided into Y-rich grains and (La, Ce, Nd)-rich grains subgroups. Two extra subgroups were created from the Fe oxides and silicate groups: the Fe-Cr-Al-rich grains (chromite) and the Zr-Si-rich grains (zircon) subgroups, respectively.

The first three (Fe-Ti oxides, Fe oxides, and silicates) were considered major groups due to the greater relative abundance of these mineral grains, and only for them was the SEM morphological characterisation (angular or rounded) taken into account (dataset SEM morphology-composition). The remaining groups were named minor, and only the composition dataset was considered in their statistical analysis.

A restriction was imposed regarding the sample size (i.e. the number of grains per sample) to improve the statistics and multivariate analysis robustness of the abovementioned samples' datasets. Samples' groups (e.g. religious house, religious order, etc.) summing up to <20 grains were not used in the corresponding statistical or multivariate analyses.

HCA was performed using the dataset (major and minor groups) described previously, applying Ward's algorithm to determine the clusters. Each dataset was composed of 15 descriptors corresponding to the percentage of grains for each mineral group (angular and rounded Fe-Ti oxides (ilmenite), angular and rounded Fe oxides (hematite), angular and rounded silicates (e.g. almandine, quartz), and Ti oxides (rutile, anatase), oxides (cassiterite), sulfide (galena), calcite, Ca-Mg-rich grains, Y-rich grains, (La, Ce, Nd)-rich grains, Fe-Cr-Al-rich grains (chromite), and the Zr-Si-rich grains (zircon)), except when any of them corresponded to a zero-sum vector. HCA was conducted over PCA scores for dimensionality reduction and standardisation over descriptors. The descriptors were pre-processed before PCA by mean centring and normalizing variance. The number of principal components used in HCA was determined based on the percentage of variance explained by each PCs. The resulting dendrogram was used to more easily rationalize sample relations to the religious house, geographical location and time period, and compositional factors correlations.

3. Results

Blotting sands were scattered generously over the fresh ink to hasten the drying process, and then the excess was removed. Nevertheless, only a small fraction of those particles would remain attached to the writing surface when the process was finished. Furthermore, over time, the handling of the document would promote the release of the looser particles from the surface of the dried ink (Fig. 2a). In a few cases, blotting sands can still be found to cover written words, either because they were more amply sprinkled over the fresh ink and the cleaning process was ineffective in removing the excess or because the sands were used with an esthetical purpose, as reported by Blake "in some cases the

Table 1
The geographical region where the houses were located, analysed volumes, time period and the number of collected samples.

Region	Location	Monastery | Convent | Religious house (religious order) ▼	Volume's reference*	No. inspected volumes	Time period	No. of samples
North	Caminha	SC (OFM)	BNP, Co. Cx.15, M1, D4	1	1786–1799	3
	Porto	SC (OFM)	ANTT, Ls: 62, 64–65, 67–71, 73, 74, 76–77, 79–81, 83–84, 86–98, 100, 104–106, 108–109	20	1630–1795	81
		SF (OFM)	BNP, Co. Cx.15, M1, D13.4	1	1811	1
Centre	Ferreira de Aves	SE (OSB)	BNP, Cod. 8448	1	1780–1797	15
	Vinhó	MD (OFM)	BNP, L34	1	1798	1
	Tentúgal	OLNT (OCarm)	ANTT, Ls: 26, 30, 33, 34–36, 38–42	11	1699–1795	19
	Tomar	T (OCist)	ANTT, L118	4	1529–1540	5
Estremadura	Alcobaça	SMA (OCist)	ANTT, Ls: 221–222, 224–227, 231	8	1721–1798	28
	Santarém	SBA (OSB)	BNP, Co. Cx. 18, D7-8	1	1759–1761	1
	Lisbon	SB (OSB)	BNP, Co. Cx. 18, D5	1	1743	1
		OLC (OCD)	BNP, Co. Cx. 8, M7	1	1762–1770	1
Alentejo	Estremoz	SJP (Hospital)	BPE, L51	3	1631	1
		OLC (CO)	BPE, Cod. CLXV/1–9		1717	1
		SF (OFM)	BPE, L4		1790–1793	1
	Borba	OLMC (OSPPE)	ADE, Cx.1	1	1744–1763	1
	Évora	CH (OSH)	BPE, Cod. CLXVII/1–10	11	1584–1712	3
		SBC (OCist)	BPE, CXXXII/1–3		1699–1772	1
		S (OFM)	BPE, L71		1700	1
		Ct (OCart)	BPE, L812		1777	2
		OLG (OSA)	BPE, Cod. CLXVII/1–10; Cod. CLXVII/1–9		1715–1757	3
		SC (OFM)	BNP, Co. Cx. 15, M1, D8		1778	1
		SMo (OSA)	BNP, Co. Cx. 8, M6		1816	3
		OLP (OP)	BPE, L21		1789–1790	1
	Beja	SC (OFM)	BNP, Co. Cx. 15, M1, D3	1	1629	1
Madeira	Funchal	OLI (OFM)	ANTT, Ls: 9–10	5	1675–1678	2
		SC (OFM)	ANTT, Ls: 1, 2, 11, 35, 37		1500–1600 | 1725–1726	7

▼ CO - Confederation of Oratories of Saint Philip Neri | Oratorians; Hospital - The Most Venerable Order of the Hospital of Saint John of Jerusalem | Order of St. John; OCarm - Order of the Brothers of the Blessed Virgin Mary of Mount Carmel | Carmelites; OCart - Carthusian Order | Carthusians; OCist - Order of Cistercians | Cistercians; OCD - Order of the Discalced Carmelites | Carmelites; OFM - Order of Friars Minor | Franciscans; OP - Order of Preachers | Dominicans; OSA - Order of the Hermits of St. Augustine | Augustinians; OSB - Order of St. Benedict | Benedictines; OSH - Order of St. Jerome | Hieronymites; OSPPE - Order of St. Paul the First Hermit | The Pauline Fathers.

*ADE - District Archive of Évora; ANTT - National Archive of Torre do Tombo; BNP - National Library of Portugal; BPE - Public Library of Évora; Co. - Collections in processing; Cod. - Codex; Cx. – Box; D - Document; L - Book, Ls - Books; M - Sheaf of documents.

Fig. 2. Blotting sands deposited on the handwritten records. Account books for a) ANTT, OFM-SC (Porto), L64, f. 139v (1644); b) BNP, Co. Cx. 15, M1, D8 (1778); c-e) OM images of loose blotting sands composed of mixtures of minerals (c) and minerals mixed with organic materials (d, e).

sparkly side effects were deliberately cultivated" [10] (Fig. 2b).

Blotting sands comprise several materials, as said previously. The sands in this study primarily include mixtures of minerals alone and are dominated by black sands (Fig. 2c); however, some are also found mixed with organic particles (Fig. 2d-2e).

3.1. Analytical characterisation of the blotting sands

3.1.1. Mineral fraction

SEM-EDS and Raman spectroscopy were combined to characterise the mineralogical composition of the blotting sands. Regardless of the region, samples were generally composed of multi-minerals that we assigned to eight groups by decreasing order of abundance: Fe-Ti oxides (i.e. ilmenite), Fe oxides (e.g. hematite, chromite), silicates (e.g. almandine, quartz, zircon), Ti oxides (i.e. rutile, anatase), phosphates (i.e. (REE)-rich grains), carbonates (e.g., calcite, Ca-Mg-rich grains), oxides (e.g. cassiterite) and sulfide (galena).

Minerals like ilmenite, hematite, magnetite, zircon, cassiterite, among many others, with specific gravities greater than quartz (s.g. 2.65) and feldspar (s.g. 2.54–2.76), the two main components of sands, are called heavy minerals [29,30]. Overall, heavy minerals account for 86% of our samples, with the Fe-Ti oxides fraction representing the highest incidence (greater than 55–70%), followed by hematite (~10–30%) and almandine (3–4%). A representative BSE micrograph of a sample from the OLG convent (Évora) with elemental maps and point analyses are exemplified in Fig. 3.

The sample mainly comprises single-mineral grains of different minerals; however, several multi-mineral grains can still be found. The Fe and Ti maps overlap, indicating that the Fe-Ti oxides (i.e. ilmenite) group is undoubtedly the most representative. Additionally, some Fe-rich grains were observed in the Fe EDS map. Other "silicate group" members, like quartz and Zr-Si-rich grains, were also identified. Finally, minor species are the grains containing Ca or Sn alone (one in each case).

Similarly to the previously gathered information concerning the samples from the Portuguese Inquisition documents [17], ilmenite, Fe oxides, and silicates were the most abundant minerals identified among the blotting sands. However, slight differences were found regarding the smaller fractions; for instance, carbonates and galena minerals were absent in the Inquisition samples. On the other hand, Milke et al. [9], in their study on blotting sands from central European countries, reported a wider variety of minerals classified into seven distinct categories, in

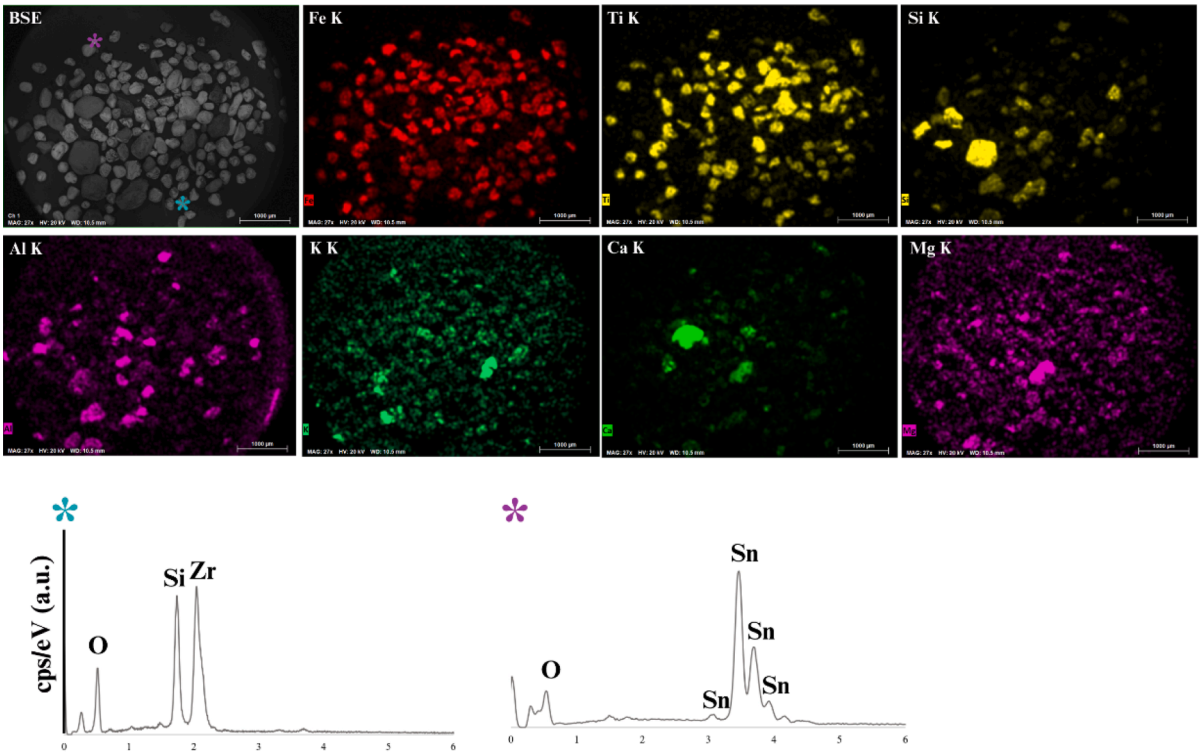

Fig. 3. Sample overview (OLG convent, Évora, Alentejo) in the BSE micrograph and respective Fe Kα, Ti Kα, Si Kα, Al Kα, K Kα, Ca Kα, and Mg Kα EDS maps. EDS point analysis in zircon (left) and cassiterite (right) grains (below).

which Fe-Ti oxides and Fe oxides were not the dominant minerals.

Transported away from the parent rock and deposited in the placer, ilmenite can undergo a progressive alteration due to chemical weathering, with iron leaching from the structure [31]. Sequentially, ilmenite alters to pseudorutile ($Fe_2Ti_3O_9$), leucoxene and finally to rutile or anatase (TiO_2) when no iron ions remain in the structure [31,32]. EDS point analysis on a few ilmenite grains evidenced this chemical alteration to lighter phases, where higher Ti wt% than the theoretical value (31.56 wt% [31]) and a decrease in the Fe wt% were estimated (data not shown).

Heavy mineral concentrates occur naturally in placers, also known as depositional environments, like beaches, stream channels, lakes, or the mouth of rivers [29,30]. However, these now studied concentrates deeply dominated by ilmenite are not commonly found in nature, suggesting that the blotting sands are an artificially assembled product.

Raman spectroscopy complemented the EDS analysis and was crucial to deepening the mineral phases' information. The dominant presence of ilmenite was once more observed in the Raman analysis. A representative spectrum for this mineral is presented in Fig. 4a and is comparable to those reported in the RRUFF™ database (RRUFF ID: R130214). According to Wang et al. [33], ten Raman active vibrational modes ($5A_g + 5E_g$) are predicted for the ilmenite mineral, of which four are recorded in our spectrum (221, 328, 369, 676 cm^{-1}). The first band (221 cm^{-1}) is assigned to the movement of Fe ion in the crystal lattice, and the bands at 369 and 676 cm^{-1} arise from the bending and the symmetric stretching vibrations of TiO_6 octahedra, respectively [32,34].

Hematite (Fig. 4a) and almandine (Fig. 4b) minerals were included in the group labelled "Fe oxides" and "silicates", respectively. Their Raman spectra agree well with those reported in the RRUFF™ database (RRUFF ID: R040024 (hematite) and X050010 (almandine)). Hematite (α-Fe_2O_3) has the corundum crystal structure consisting of a hexagonal close packing of oxygen atoms, with Fe atoms in two-thirds of the octahedral sites [34]. This mineral shows seven characteristic Raman-active vibration modes ($2A_{1g} + 5E_g$) attributed to the motion within the FeO_6 octahedral unit and rotations and translations of the Fe_2O_3 unit [34]. Five of these (219, 287, 407, 497, and 607 cm^{-1}) are observed in our spectrum (Fig. 4a).

Almandine ($Fe_3Al_2(SiO_4)_3$) is the end member of the Fe-Al garnet solid solution. Substitution of Fe in the dodecahedral sites by elements like Mg or Ca leads to the pyrope ($Mg_3Al_2(SiO_4)_3$) or grossular ($Ca_3Al_2(SiO_4)_3$) end members, respectively, with solid solutions series between the end members [35–38]. The Raman band shifting can then be used to explain changes in chemical composition [37]. According to the literature [36,37,39], bands in the distinct regions of the spectra can be assigned as follows: 160–170 cm^{-1} to divalent cations (Fe^{2+}, Mg^{2+}, Ca^{2+}) translational modes, 210–250 cm^{-1} to the translational motion of SiO_4 tetrahedra, 310–420 cm^{-1} to the rotational modes of SiO_4 tetrahedra, 460–640 cm^{-1} to the O—Si—O bending modes (ν_2 symmetric and ν_4 antisymmetric), and 850–1100 cm^{-1} to the Si—O stretching modes (ν_1 symmetric and ν_3 antisymmetric). Wavenumber shifting can be observed for the Si—O vibrations of the SiO_4 tetrahedra due to several factors influencing the position of the Raman bands, namely, the atomic mass, cation charge and ionic radius, with the latter having the most substantial effect [37,40].

In this respect, a closer look at our Raman almandine-garnet results (Fig. 4b) evidenced that different compositions for distinct grains can be inferred. The increasing ionic radii from Mg^{2+} to Fe^{2+} and Ca^{2+} downshifted the ν_1 symmetric stretching band. The two topmost spectra are close to almandine since the bands assigned to the Si—O stretching mode (914 cm^{-1}), the rotational modes of SiO_4 tetrahedral (370, 343 cm^{-1}) and translational modes of divalent cations (168 cm^{-1}) are in accordance with the literature for almandine-rich garnets (916, 372, 347, 167 cm^{-1}) [39]. The band at 354 cm^{-1} is upper-shifted in the bottommost spectrum compared to the previously discussed spectra. A slight shift from 914 to 918 cm^{-1} was also observed in the region assigned to the ν_1 symmetric stretching Si-O mode, suggesting that the bottommost spectrum corresponds to a mineral close to pyrope-garnet (higher MgO content) [40]. Moreover, the band at ~370 cm^{-1}, present in the almandine-rich garnets and absent in the pyrope-garnets, is not prominent in this spectrum, supporting the pyrope-richer garnet

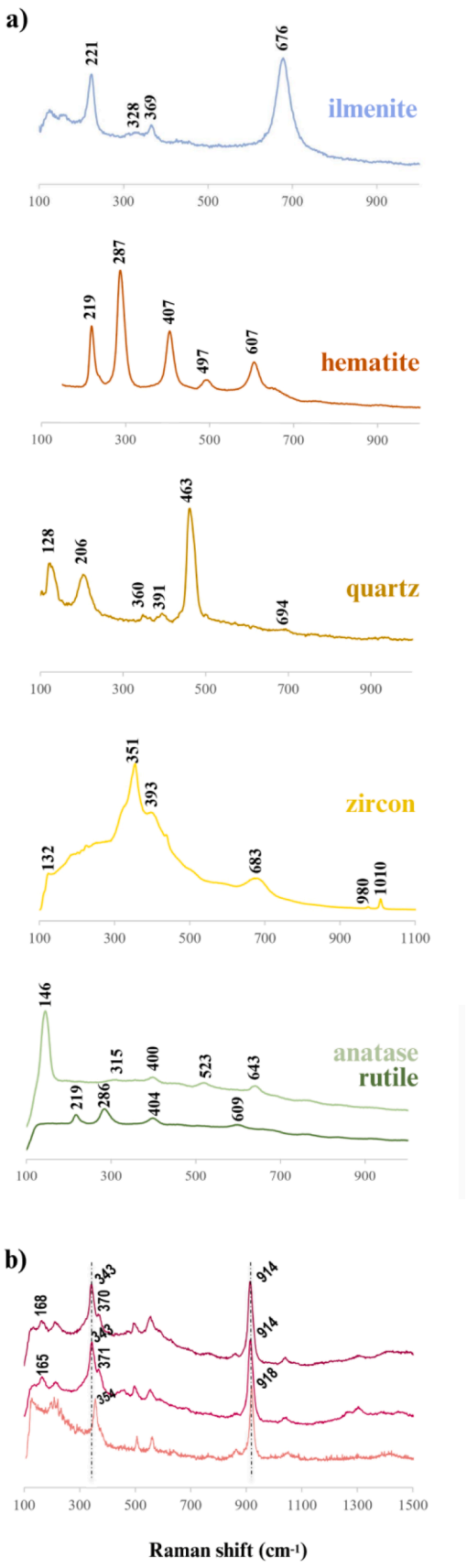

Fig. 4. Raman spectrum (from top to bottom): a) ilmenite (SC monastery (Porto, 1672), hematite (SE convent, Ferreira de Aves, 1777), quartz and zircon (SC monastery, Caminha), 1799); anatase and rutile (SBC convent, Évora, 1699–1772); b) almandine (SC monastery, Funchal, 1500–1600).

hypothesis in these grains. Lastly, the band at ~165 cm^{-1} is absent, as observed in minerals chemically closer to pyrope [40]. Furthermore, EDS point analysis reinforced this discussion (data not shown). In a few Fe-Al-Si-rich grains, the EDS spectra showed the presence of Mg-Al-Si elements, suggesting the substitution of Fe by Mg ions in the almandine-pyrope series. Ca-Al-Si sequence was also detected on EDS analysis of some grains, indicating the enrichment in grossular garnets [37,41].

Quartz and zircon were also corroborated for the silicate group. Crystalline quartz was confirmed by the characteristic band at 463 cm^{-1} [42] (Fig. 4a). The Raman spectrum of the Zr-Si-rich grains presented bands at 132, 351, 393, 683, 980, and 1010 cm^{-1}. As documented [43], the 400–600 cm^{-1} region corresponds to the O—Si—O bending vibrations, the 980 cm^{-1} band is assigned to the symmetric SiO_4 stretching vibrations, while the ~1008 cm^{-1} band is associated with the anti-symmetric stretching of SiO_4 [43,44].

Raman spectroscopy was fundamental to distinguishing minerals in the Ti oxide group as rutile and anatase (Fig. 4a). Our rutile spectrum consisted of four characteristic bands (140, 219, 404, and 609 cm^{-1}) corresponding to four of this mineral's five Raman active modes [45]. Anatase presented five bands at 146, 315, 400, 523, and 643 cm^{-1} for five over six Raman-active modes [45]. A resume of the Raman shifts and respective assignments based on the literature is presented in Table SM.2.

Some minerals less abundant in major groups or belonging to minor groups were also analysed. Identification was done based on the RRUFF™ database and the literature [37,46–48]. Representative spectra of some of these minerals are presented in Fig. 5. Chromite, included in the Fe oxide group, was only identified in three samples from different houses: SC monastery (Évora, Alentejo, 1778), SMA convent (Alcobaça, Estremadura, 1726), and OLI convent (Funchal, Madeira, 1675–1678), with a relative frequency of occurrence of ~3%, 7%, and 8%, within the total amount of grains per sample (data not shown).

Another example for the minor mineral groups includes the REE-rich grains, from the phosphate group, with variable %wt. of the elements Ce, La, and Nd. Tundrite, although identified in a few samples from all the regions, comprised only <2% of the sample content. Xenotime is another REE-mineral identified in a similar context (Fig. 5).

Calcite (Fig. 5) was predominantly observed in samples from the Alentejo region, in SB (1699–1772), Ct (1777–1778), OLG (1757) convents in Évora and OLC in Estremoz (1777–1780). It also appeared in two samples from the SC monastery (1550–1600) in Madeira Island and one from the SC monastery in northern Portugal (Porto, 1771). In our previous study [17] on the blotting sands, calcite was not identified, suggesting that this mineral was seldom included in the blotting materials in Portugal.

Cassiterite (Fig. 5) appeared in one sample from the SMo, OLG, and Ct convents in Évora and two from the OLNT convent in Tentúgal, Centre (1754).

Closing this group of minor minerals is galena (Pb-rich grains). Its identification was made by EDS analysis since no Raman spectrum was obtained. It was only detected in around 2% of the samples collected: in two from SE (Ferreira de Aves, Centre), one from SMA (Alcobaça, Estremadura), and one from SC monastery (Caminha, North). The EDS spectrum is illustrated in Figure SM.1.

In Milke's work [9], REE-rich grains (e.g. xenotime) and calcite were among the reported minerals composing the blotting sands. However, chromite, cassiterite, and galena were not mentioned. Besides, we have documented [17] that in the Portuguese Inquisition samples, minerals like chromite and cassiterite were also scarcely identified in minor fractions, while galena was not found.

3.1.2. *Organic fraction*

While minerals were found to be the main component of the blotting sands, organic materials were also identified, constituting entirely new data in the Portuguese context. Indeed, only minerals were found in the

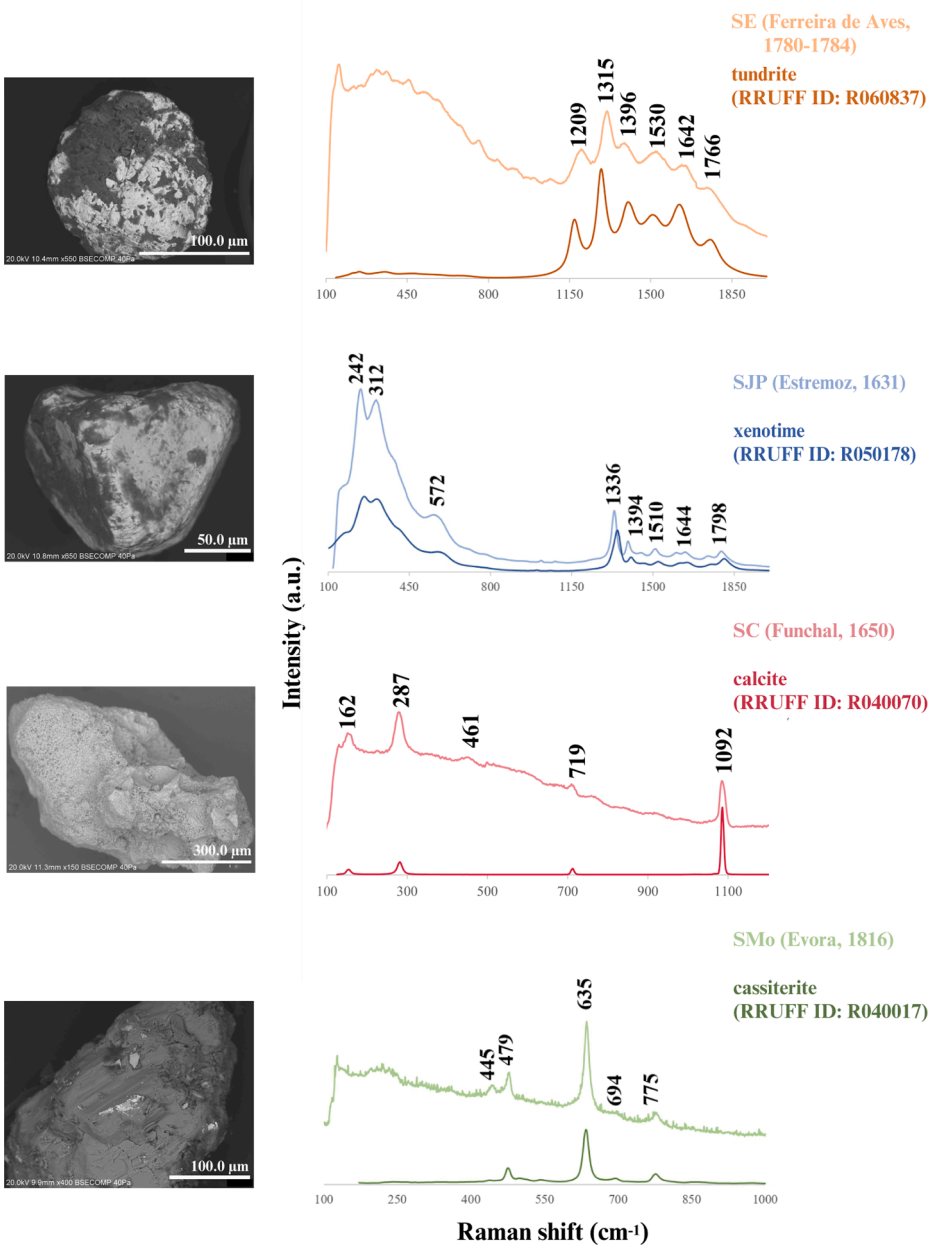

Fig. 5. BSE micrographs of representative samples and respective Raman spectra (light colours) with corresponding RRUFF™ database spectra (dark colours).

blotting sands in the documentation from the Portuguese Inquisition in the same time period approximately [17].

In eleven samples, the non-mineral particles were mixed with minerals. Two different types of particles were observed: small-sized (~0.50–0.80 mm), yellow-coloured, brownish particles with irregular shape (Fig. 6a), and same-sized, smooth, whitish cocoons (Fig. 6b), seeming both to be organic. FT-IR spectroscopy, the technique selected for organic materials characterisation, confirmed the yellow-coloured materials as gums and the smooth cocoons as paper. Bone shavings (Fig. 6c) were mixed with minerals in other samples. The summary of the materials identified is presented in Table 2.

The spectrum referring to the gum (Fig. 6a) presented a broad absorption band in the region ~3300–3280 cm^{-1} (νO—H) and bands at about 2890 cm^{-1} (νCH_2), 1648 cm^{-1} (νCOO), 1426 cm^{-1} (δCH_2 and δCH_3), 1369 cm^{-1} (δCH_3) and 1060 cm^{-1} (νC—O—C) characteristics of a gum [49]. The comparison of the assigned bands with the reported data may suggest the use of Arabic gum [49]. As to the smooth, whitish particles, the typical spectrum for cellulose was obtained (Fig. 6b), showing absorption bands at 3324 cm^{-1} (νO-H), 2897 cm^{-1} (νCH_2), and the characteristic bands in the range 1400–900 cm^{-1} associated to the cellulose fingerprint region [50]. The bands at 1428, 1352, 1027, and 889 cm^{-1} were assigned to δCH_2, δCOH in-plane, νCOC pyranose ring vibration, and νCOC at β-glycosidic linkages [50].

The gum particles were observed in all the samples containing organic materials. However, they generally constituted a minor fraction, except for two samples from the SB convent (Lisbon, Estremadura) and the SC monastery (Funchal, Madeira), mainly composed by them. On the other hand, the paper cocoons were found in five samples from Madeira Island and Beja, comprising a maximum of 50% of only two samples (SC monastery, Funchal). Bone shavings (Fig. 6c) were found in residual amounts in two samples, one in mainland Portugal and the other from Madeira Island.

Although paper cocoons and gum particles were found in only 6% of the samples, they were observed in large amounts, suggesting that they were purposely added. These materials, plus bone shavings, can act as absorbents for excess ink. Maybe the religious houses lacked mineral

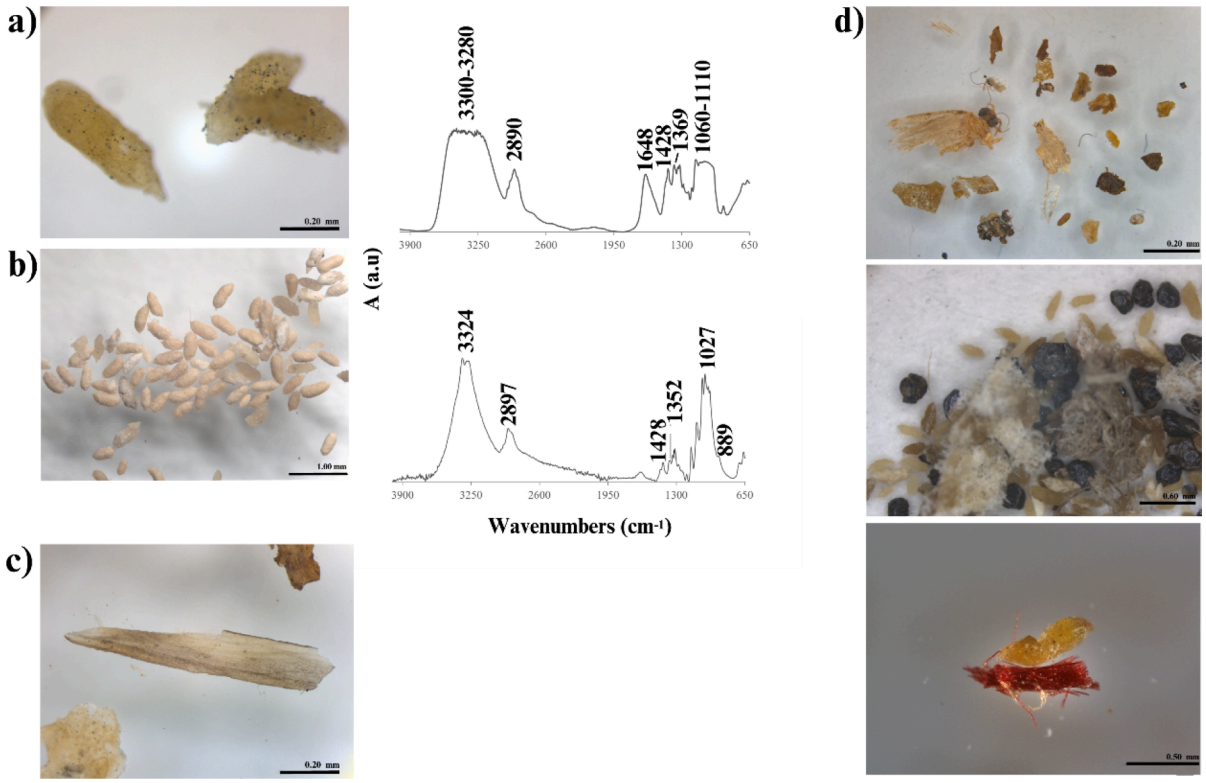

Fig. 6. OM images and corresponding FT-IR spectra for organic materials on blotting sands: a) gum particles from SMo convent (Évora, Alentejo); b) paper cocoons from OLI convent (Funchal, Madeira); c) bone shavings; d) pieces of waste materials such as insects (left) and textile fibres (centre and right) that were not intentionally added to the blotting sands (SE convent, Ferreira de Aves, 1796–1797).

materials that increased the surface area of the fresh ink and had to include some absorbent materials to ensure the excess ink was removed. Another explanation can be supplied for the presence of gums. The paper surface was previously prepared to be used as a writing support. To improve the writing quality, sandarac - and not usually Arabic gum, although it could be chosen - was employed in a procedure known as pounce [10,51]. The gum was powdered and deposited over the writing surface. Then it was gently buffed to soften and uniform the surface by filling the gaps, which helped to prevent the bleeding of the writing ink [52]. Hence, it is possible that some particles remained on the surface in a few cases and were mixed with the blotting materials.

3.2. Spotlight on the minerals

3.2.1. Grain-size distribution and shape features

Minerals' grain size ($\bar{D}_F$) in blotting sands from the five regions showed that it spanned from 0.06 0.01 to 1.70±0.04 mm, with average values per region falling into the first third of the medium range (0.250–0.500 mm) in the Wentworth's grain scale.

Table 2
Location of the religious houses and time period, non-mineral materials identified in the blotting sands and the no. of samples where they were observed.

Region	Location, convent | monastery	Time period	Type of materials	No. samples
Centre	Ferreira de Aves, SE	1778	gum, bone shavings	1
	Vinhó, MD	1798	gum	1
Estremadura	Lisbon, SB	1762–1770	gum	1
Alentejo	Évora, SMo	1816	gum	3
	Beja, SC	1629	gum, paper	1
Madeira	Funchal, OLI	1675–1678	gum, paper	2
	Funchal, SC	1500–1600	gum, paper, bone shavings	2

Except for Madeira's region, medium-sized sands were found in the highest relative proportion. Fine sands represent <26% in the North and Centre regions and around 33–35% in the Estremadura and Alentejo in the country's southern half. Madeira Island introduces a difference in this trend since the fine sands' fraction dominates the samples with a slightly higher value than 50%. This fraction plays a critical role in the grain size average, decreasing it to the lowest value found in the country. Within the error, the grain size average is undoubtedly smaller from the North, Centre and Estremadura regions. Interestingly, the Alentejo region in mainland Portugal has the highest fraction (97%) of grains belonging to medium or lower classes and the average closest to Madeira's. Samples from the North and Estremadura regions included the highest content of coarse grains, 8.5% and 5.9%, respectively. Very fine and very coarse grains corresponded to less-frequently occurring classes (≤2%).

Table 3 resumes the grain size average ($\bar{D}_F$) and the relative abundance (%) within the Wentworth classes per region, and Fig. 7a illustrates the grain size distribution per region.

Globally, the grain size distribution showed a very similar trend within the regions, with a near-symmetrical unimodal distribution and a near-constant median (Fig. 7a).

These results coincide well with those reported by Milke [9], suggesting that the sands were selected through a mineral processing technology, such as sieving. Moreover, we found similar distributions regarding blotting sands from the Portuguese Inquisition documents [17], reinforcing the processing hypothesis.

Grains' morphology was evaluated using two shape parameters assessed with ImageJ® software – roundness (R) and circularity (C). The average values of these parameters per region are detailed in Table 4.

The blotting sands in mainland Portugal are similar, concerning the sharpness of the grain corners (R values), with the average values within the well-rounded class. The R values distribution (Fig. 7b) follows the same trend, with a broad range of values spanning from approximately

0.4 to 1.0. Madeira samples showed a distinctive bimodal distribution, from approximately R=0.1 to R=0.8.

As to the C parameter, the average values fall into the range of 0.70–0.83, with the grains presenting high circularity. The Alentejo and Estremadura regions tend to favour slightly more circular grains (Table 4). Differently, Madeira Island showed the lowest R and C average values, much closer to the angular classes and less circular grains. The frequency distributions for the C parameter (Fig. 7c) referring to the mainland regions present a similar general shape for the violin plots, slightly skewed to high values. Although not very pronounced, differences at the maximum frequency position can be observed, especially when comparing the North to the Alentejo regions. As for R, Madeira differs substantially from the mainland. The distribution is clearly bimodal, with a maximum close to C=0.70 and a small fraction of the samples showing similar behaviour to continental Portugal.

3.2.2. *Chasing trends - a statistical and multivariate approach*

- **in the country**

Based on SEM observation and EDS chemical analysis, an overlook on the blotting sands per region for the major groups of minerals (Fe-Ti oxides, Fe oxides and silicates) allowed us to draw some interesting conclusions (Fig. 8).

The samples of the religious houses (SC, Porto and Caminha; and SF, Porto) in the North of Portugal showed a similar overall mineralogical composition with contributions from the three major groups, except for the SF house, where no silicates were found. Regarding the minerals' morphology, differences can be pointed out. Blotting sands between 1651 and 1750 were sampled only from the SC Porto monastery, showing a completely different behaviour regarding the average proportion of angular ilmenite. In the first fifty years, angular ilmenite comprised around 45% of the samples, whereas in the second fifty-years period, it was <5%. On the other hand, Fe oxides increased in the latter, with a more significant proportion of angular Fe oxides.

In their transport from the parent rock to placers, where the sediments lay down in layers and concentrate, the debris' morphology suffers alteration towards a higher roundness and sphericity due to the physical interactions [53,54]. The effects of these interactions depend on the chemical composition, crystal lattice and transport distance of the rock fragments [54]. Once the sands are deposited, the process continues over time. Rounded and well-rounded grains are associated with medium to long-distance transport and agree with to the so-called "mature sediments"[53].

The higher percentage of angular ilmenite for the second half of the 17th century found in the North region suggests that the SC monastery either was using blotting sands from a placer fed by two different sources concerning the grains maturity or the sisters of St. Claire (SC) were mixing blotting sands from different origins in their sanders.

A more contrasting behaviour associated with the presence of the major groups and their maturity was observed for the Centre region. OLNT convent, for example, over 100 years, used differentiated blotting sands in composition and morphology. In the earliest period, samples only included ilmenite and Fe oxides, with a shape compatible with mature sediments. Conversely, ilmenite later dominated samples from 1701 to 1750 (~90%), but the remaining 10% varied more in composition, with more mature sediments (Figure SM.2). It is clear that for 100 years, the Carmelite sisters from the OLNT convent sprinkled blotting sands collected from distinct sources over their account books. Another interesting example is given by the SE and MD houses, geographically close in time (1751–1800) and space (50 km away), with ~70% of angular ilmenite and galena as major and minor components (Fig. 7 and SM.2). These characteristics were not found in the blotting sands from other houses in the Centre region, suggesting that both houses were probably buying blotting sands gathered in the same area, with a more substantial contribution of less mature ilmenite.

Due to the constraints on the number of grains, only the SMA monastery from the Estremadura region was studied. Over time, an interesting similarity in the composition and morphology of the blotting sands' major components is seen. Minor fractions show some differences but comprise a 5% maximum of the samples (Figure SM.2). Considering the geographical context of the SMA monastery (Estremadura), the sedimentary deposits in the Tagus River, enriched in heavy minerals, can be pointed out as a good candidate for the blotting sands' source.

Alentejo region was the one presenting the wider compositional variability per sample over time, with the minor groups contributing importantly to it (Figure SM.2). This is particularly evident for the OLG convent (1751–1800) and SC monastery in Beja (1751–1800), with ~11% and ~17%, respectively, in minor components. Besides, considering the major groups, contrasting results were found between the earliest (1501–1550) (CH convent, Évora) and the latest samples (1801–1850) (SMo convent, Évora), in which the former includes only rounded grains, while the latter is dominated by angular ilmenite (~70%). Undoubtedly, the monks of St. Jerome (CH) in the 16th century and the sisters in the St. Monica convent (SMo) in the 19th century, both in Évora, were using blotting sands from different sources. The overall similarity in the major fractions composition and morphology for the SC (17th century, Beja), OLC, OLMC, SBC and Ct blotting sands opens the possibility that sands were collected from the same or similar sources over time (16th–18th centuries), with occasional changes. Moreover, on average, this region showed the highest fractions of Fe oxides and silicates in the country for the major group and calcite for the minor. Since most silicates, like quartz, are not heavy minerals, their systematic presence may suggest a different approach in this region, with a probable less careful selection of the blotting sands.

Madeira stands out by the predominance of angular ilmenite. Besides, it also has the lowest variability in the minor groups, with chromite (<4%) in the OLI convent and calcite (~6%) in the SC monastery. Both houses, separated by half a century, present the same blotting sand composition and morphology on average, indicating that local sources must have been used. In fact, igneous rocks, mainly composed of Fe-rich minerals such as magnetite, hematite, and ilmenite, are widely prevalent in Madeira Island [55]. Besides, the transport distance that the sediments undergo from the parent rocks to the placer deposits is shorter than those in continental Portugal, explaining the dominance of angular ilmenite.

- **in the 18th century**

Table 3
Grain size average based on the ($\bar{D_F}$) and std values and relative abundance (%) within the Wentworth classes [20] per region.

Region	grain size ($\bar{D_F}\pm\sigma$)	(%) class					no. grains
		Very fine	Fine	Medium	Coarse	Very coarse	
North	0.33±0.10	1.9	23.6	65.7	8.5	0.3	7277
Centre	0.31±0.12	0.3	25.5	71.7	2.4	0.1	4545
Estremadura	0.31±0.11	0.1	33.0	60.7	5.9	0.3	1220
Alentejo	0.29±0.09	0.7	35.7	60.6	3.0	–	5076
Madeira	0.27±0.12	1.8	51.2	42.6	4.0	0.4	1139

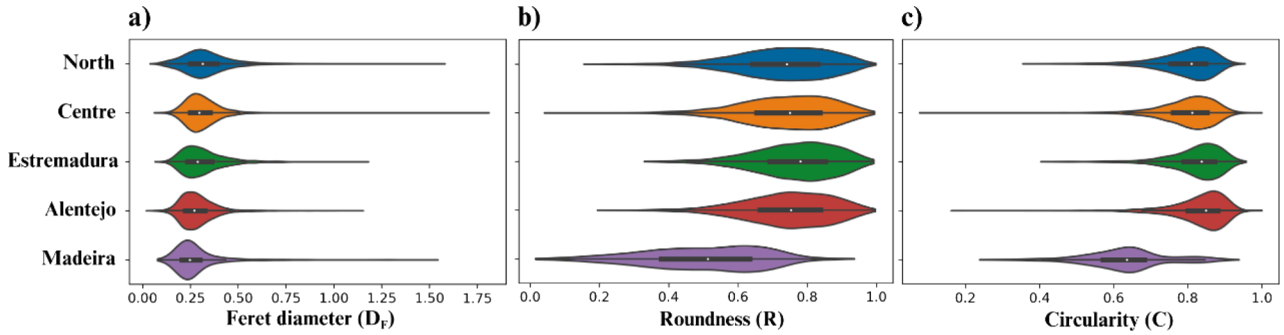

Fig. 7. Violin plots for the grain size and shape parameters distribution per region.

Table 4
Average and std values for the morphological parameters per region.

Regions	$\bar{R} \pm \sigma$	$\bar{C} \pm \sigma$
North	0.73±0.13	0.79±0.07
Centre	0.74±0.12	0.79±0.08
Estremadura	0.76±0.11	0.82±0.07
Alentejo	0.74±0.12	0.83±0.07
Madeira	0.57±0.17	0.70±0.11

To chase trends in a particular period, we took a closer look at the 18th century, where a large diversity of religious houses and samples can be found. Fig. 9 shows the dendrogram resulting from the HCA and corresponding PCA scores and loadings. The barplots resuming the minerals' relative frequency of occurrence for this century are presented in Figure SM.3.

In the yellow cluster, three samples show a good correlation: SE (Ferreira de Aves), MD (Vinhó) and SC (Caminha). SE and MD houses stand out for a very high percentage of angular ilmenite and galena. The dendrogram (Fig. 9a) resulting from the scores of the three first PCs of the PCA analysis positively related the samples with 30.3%, 19.5%, and 11.5% explained variance for PC1, PC2 and PC3, respectively (Fig. 9c). SC (Caminha) samples are also positively correlated due to the high Ti oxides content (Figure SM.3).

Another group of geographically related samples is marked green in the dendrogram, clustering samples from Alentejo (SBC (Évora), OLC (Estremoz), and OLG (Évora)) with very negative values of PC1 and PC2 scores (Fig. 9b). According to the loading map (Fig. 9c), the clustering is attributed to a similar composition in the major components and calcite.

In this time period, chemical composition clusters including Alcobaça, Tentugal and Porto are formed (violet cluster). In this cluster, Alcobaça (SMA) samples are very well correlated during the century due to the positive correlation in the PC2 score but on opposite sides of PC1.

In brief, it was possible to establish some correlation between samples from houses geographically closer, suggesting that the blotting sands could have been collected locally from the same or similar placers in composition and morphology. Besides, the lack of correlation between the houses from the same religious order confirmed that there was no centralised acquisition system with a distribution network supplying the various religious houses spread in the country.

4. Final remarks

Blotting sands is an intriguing material that frequently falls from old books when handled. Like in most of the written scripts, these sands were essentially used to hasten the drying time of the fresh ink. Religious orders have been fundamental in fostering culture and literacy in Portugal. The account books from the religious houses are essential data sources on daily activities and purchases, as well as invaluable repositories of the blotting sands used in each monastery or convent.

In this work, we have investigated the blotting sands used by the religious houses scattered across continental Portugal and Madeira Island. These sands are mainly composed of mixtures of minerals and are dominated by black sands. In some samples, minerals are mixed with organic materials, constituting a novelty in the Portuguese context since only combinations of minerals were found in previous work on samples from the General Council of the Portuguese Inquisition.

Ilmenite is the most representative mineral but others, such as hematite, and other silicates (e.g. almandine, quartz), were identified. Ti oxides (rutile and anatase), zircon, REE-rich grains, chromite, and calcite, among others, are minerals also found in a lower frequency of occurrence. Similar results were obtained for the blotting sands in the Portuguese Inquisition documents. However, this limited mineralogical variability contrasts with the reported for other European countries (e.g. Germany and Switzerland). This mineral assemblage enriched in ilmenite seems to be a preference in the Portuguese context, where a taste linked to the properties of the materials, namely colour and shine, can not be discarded.

Blotting sands were primarily medium-sized and mainly texturally mature sediments (presenting round to well-round shapes with high circularity). Madeira Island introduces a clear difference in these trends. Samples showed a distinctive bimodal distribution, tending to be smaller-sized and much closer to the angular and less circular shapes. Due to the geological-geographic context, sediments experienced shorter transport distances, i.e., less mature sediments were used to prepare the blotting sands on the island.

The morphology of the ilmenite grains in mainland Portugal strongly points out a more or less long sedimentary transport. In this sense, the placer(s) where these concentrates were explored should correspond to a sedimentary deposit (alluvial) in detriment to igneous rocks, involving complex processing for mineral concentration. Alluvial deposits containing ilmenite are mainly located in the central and northern regions of the country, predominantly in the Guarda district (Centre region). The relevant deposits in southern Portugal of São Torpes (Sines) and Santa Fé (Faro) are two exceptions. For the Alentejo region, only an alluvial/eluvial deposit of Ti is found near Santa Eulália. Still, minor unidentified occurrences of Ti cannot be ruled out, nor the presence of ilmenite as a by-product of gold exploration in an alluvial deposit.

Hierarchical group analysis showed the formation of some clusters mainly explained by compositional similarities associated with morphological aspects. Some specific cases highlighted that blotting sands could have been collected from similar placers for houses in the Centre region or Évora and Estremoz (Alentejo region). On the other hand, no centralised acquisition and distribution processes occurred within the houses of the same religious order.

Blotting sands were goods used in the writing practice, and the historical view ought to highlight this relevant material. Here, we have uncovered that the religious houses systematically ordered blotting sands. Based on this, we argue that its purchase should be included when dealing with the writing practices of European countries. Moreover, data such as the type of materials, quantities, trade units, costs, and prices should be mirrored within these materials' history.

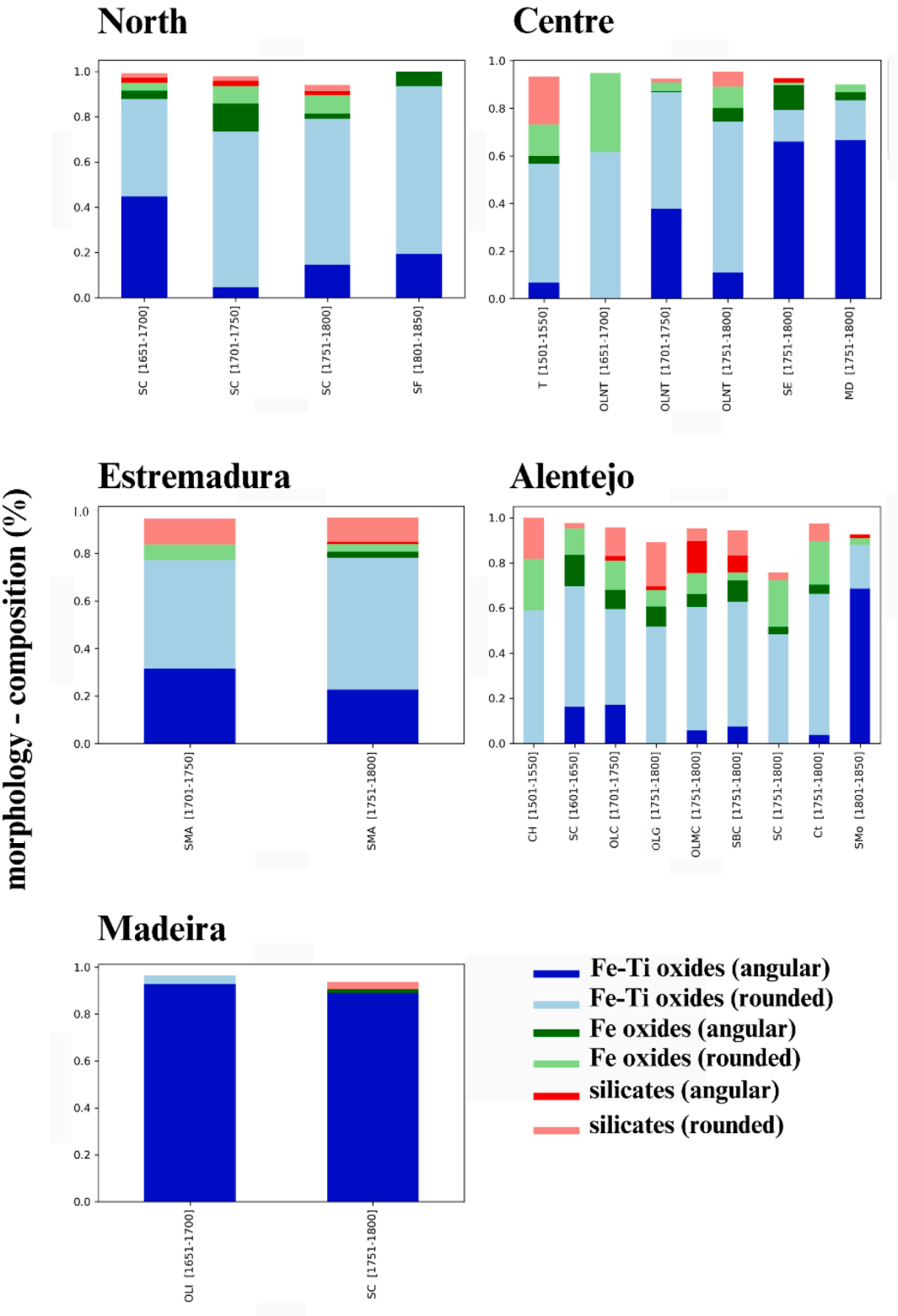

Fig. 8. Minerals' relative frequency of occurrence per religious house and time period distributed by five geographical regions based on SEM morphology-composition dataset (major mineral groups).

Not only the historical value of this writing tool is demonstrated in this work, as the existence of a specific knowledge based on established technological processes backed its production to obtain singular materials that answered a practical and aesthetical demand. The way to complementary and European-expanded historic and laboratorial research on this forgotten writing tool is now paved.

Besides, the conservation aspects of the blotting sands and the writings they are attached to are of utmost concern. Blotting sands were used with iron gall inks, which often have a deleterious effect on paper over time, making it more fragile. Additionally, the heavy sands tend to increase the brittleness of the paper support. We hope this work can contribute to a more informed and knowledgeable conservation action

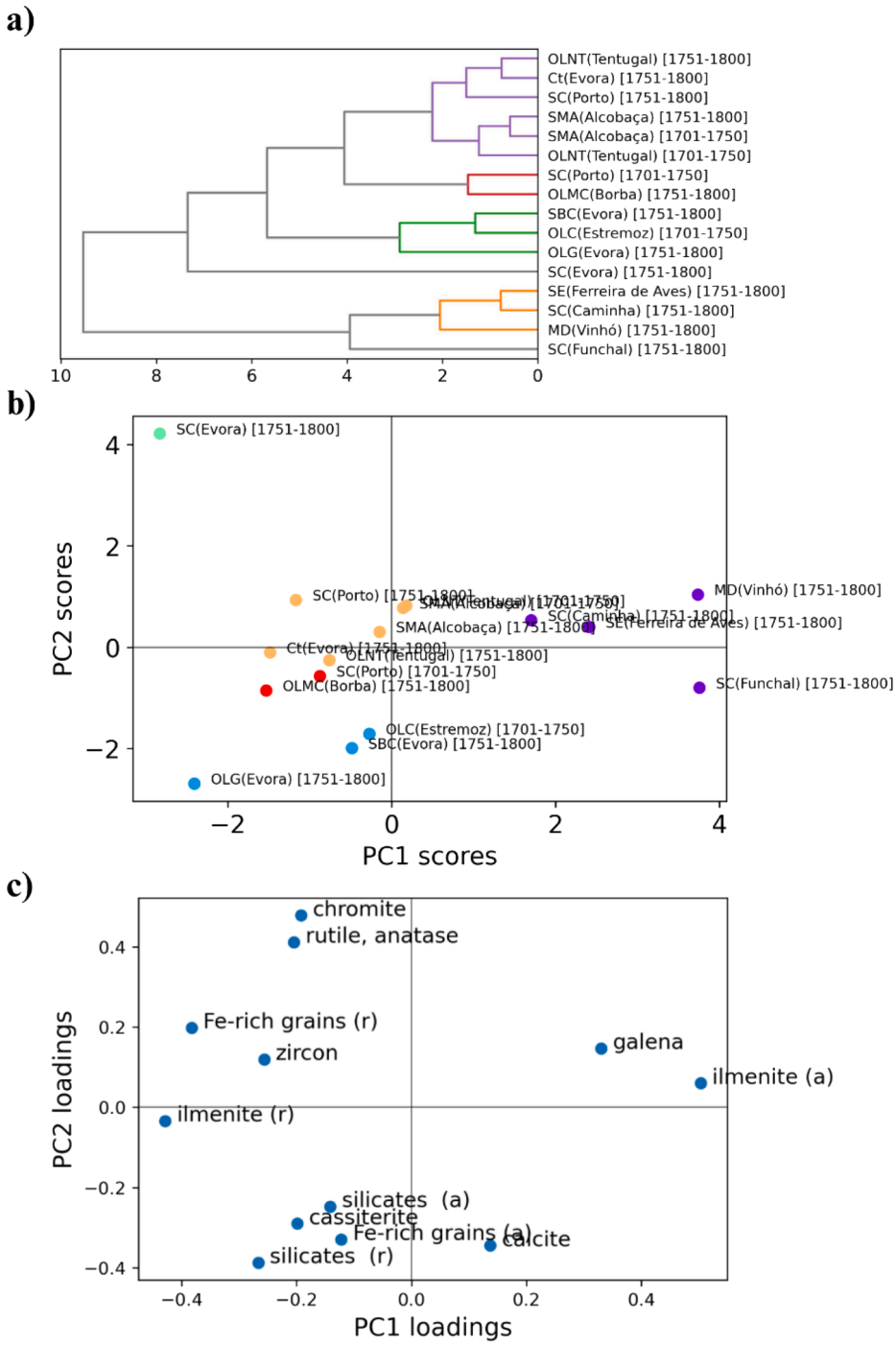

Fig. 9. a) HCA dendrogram relating 18th century religious houses as described by the mineral composition of the blotting sands; b) scores for PC1 and PC2 in the PCA analysis (points coloured highlighting the groups obtained by HCA); c) loadings for PC1 and PC2 for the PCA analysis.

regarding the written heritage.

CRediT authorship contribution statement

M. Nunes: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Visualization, Writing – original draft. **G. Wanzeller Martins:** Investigation, Formal analysis, Data curation. **J. Sarraguça:** Software, Formal analysis, Validation. **F. Olival:** Writing – original draft. **P. Moita:** Conceptualization, Methodology, Writing – review & editing. **Scott G. Mitchell:** Writing – review & editing. **A. Claro:** Conceptualization, Methodology, Writing – review & editing. **T. Ferreira:** Conceptualization, Methodology, Writing – original draft, Supervision, Writing – review & editing.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

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