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Discovering manganese-based blacks in the grave goods of Kha and Merit (Egypt, 1450-1400 BCE): Multidisciplinary investigation on use and nature

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ABSTRACT

As part of the "TT8 Project", several research groups examined the grave goods from the Theban Tomb No. 8 of Kha and his wife Merit who lived during the second half of 18th dynasty and were discovered by the Italian Archaeological Mission led by Ernesto Schiaparelli. Thanks to the collaboration of Egyptologists, conservators, and scientists, numerous state-of-the-art, non-invasive methods were used to examine and characterize the objects found in the tomb.

During this comprehensive investigation, for which a fully non-invasive approach was designed, the preliminary results for three polychrome wooden caskets showed the unexpected presence of manganese in the black areas in combination with the carbon black ink also present in the black decorations.

In addition to MA-XRF analysis, which allowed for the discovery, an innovative imaging method was applied for faster discrimination of black pigments. This method is based on the optical spectral differences between manganese-based blacks and carbon black in the short-wave infrared – with a maximum difference in the range of 1400–1700 nm – and is comparable to a photograph in terms of acquisition time. By using an InGaAs camera with an interferential long-pass filter of 1400 nm, the images were acquired first on a series of mock-ups and then on the wooden caskets. Using false color imaging representation, the areas painted with manganese black showed a clear red false color, in contrast to the black false color of the areas painted with carbon black. The results are fundamental to understanding whether the use of manganese black could be more widespread than reported in the literature so far.

1. Introduction

Modern Egyptology integrates scientific methodologies and conservation techniques through a collaborative and interdisciplinary approach, aiming to unravel the complexities of ancient Egyptian civilization. By leveraging bibliographic investigations and advanced analytical methods, researchers can extensively examine the raw materials and technologies used in the creation of cultural artifacts, thereby reconstructing the materials and techniques known and available in antiquity. This research also enables the identification of recurrent production techniques employed in ritual objects, which are considered as products of craftsmanship rather than individual artistic expressions. The rediscovery of these techniques offers a retrospective journey into the traditions and technologies of a distant and captivating era. Additionally, through the comparison with excavation and conservation documentation, it becomes possible to identify non-original materials added during previous conservation interventions, thus providing insight into the most recent information of an object's history.

The study of colored materials, particularly pigments, is of significant interest, given the remarkably diverse palette used in Ancient Egypt over 3500 years. This vast array of pigments necessitates a comprehensive understanding of their recipes, contexts of use, and painting techniques. Notably, despite the technological limitations of the period, some Egyptian pigments were synthetic, such as Egyptian blue and Egyptian green, while others were used as cosmetics for the body and hair. Scott's review offers a detailed chronology and analysis of materials used by the Ancient Egyptians [1].

On February 15, 1906, Arthur Weigall and Ernesto Schiaparelli, representing the Italian Archaeological Mission, discovered the intact Tomb of the Royal Architect Kha and his Spouse Merit in an eastern Theban valley near the ancient worker's village of Deir el-Medina [2]. This discovery is regarded as one of the most significant in ancient Egyptian archaeology, representing the most extensive and complete non-royal burial assemblage ever found. The artifacts from this tomb, now displayed in a dedicated hall of the Museo Egizio in Turin, have recently been subjected to an interdisciplinary research project initiated

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in 2017 named TT8 (Teban Tomb 8). This project, involving collaboration among scientists, Egyptologists, conservators, archivists, and archaeologists, aims to conduct a comprehensive study of the Theban Tomb 8, utilizing archaeological, historical, cultural, and conservation data. Continuing the work initiated in the last decade, the Museo Egizio in Turin has increasingly focused on non-invasive analyses, driven by the need to expand the investigation framework to whole classes of objects, materials, and collections. By studying classes of objects, researchers can identify patterns and variations that might not be apparent when only examining individual pieces. This holistic approach enhances the overall knowledge of ancient Egyptian material culture and its technological practices, enlightening us with a more comprehensive view. Destructive analyses can indeed cause irreversible damage and should be used only as a last resort, given the irreplaceable nature of many items in the museum's collection and the necessity of preserving their physical condition. Furthermore, the museum's dedication to non-destructive analysis not only preserves its collections but also establishes best practices and protocols that can be shared with institutions worldwide. The TT8 project was developed in this context, involving various research groups with the aim of characterizing different objects and their constituent materials using non-invasive, state-of-the-art instruments and analytical methodologies. This paper specifically examines black pigments, prompted by the discovery of manganese-based blacks on artifacts from Kha and Merit's tomb during a Macro X-ray fluorescence (MA-XRF) imaging campaign [3]. The objects, previously unexamined, provide an invaluable opportunity for a holistic investigation.

In Ancient Egypt, the predominant black pigments were carbon-based, produced through charring plant materials (charcoal), soot (lampblack) [4], or animal bones (bone black) [5]. These were commonly used in texts on papyri and ostraca or on coffins, typically mixed with gum Arabic binder [1]. Besides carbon-based pigments, other black materials, such as iron gall ink or sepia, primarily served as writing inks [6,7]. However, manganese black, although rare and less understood compared to carbon black, was also used.

Early reports by Lucas and Harris documented the use of manganese black in New Kingdom wall paintings at Bani Hassan [8], and Middleton confirmed its presence in the tomb of Djehutyhotep at Al-Bersheh and on Middle Kingdom coffins [9,10]. Takahashi et al. identified manganese black used to darken Egyptian blue in the Royal Tomb of Amenophis III [11], and it was also found in early glass production [12]. Manganese blacks, primarily composed of pyrolusite (MnO_2), were sourced from areas such as Sinai and the Eastern desert and sometimes combined with lime to create grey shades, as seen in the tomb of Ramose in Thebes [13]. Pyrolusite was also used in artifacts from Lower Egypt and as eye paint in the Predynastic site of Maadi [1,14–16]. The presence of manganite, another manganese oxide-hydroxide mineral, indicates the extensive mining and utilization of these resources by the Egyptians [17–20].

Egyptian manganese ores are abundant, notably at Um Bogma in the Central Western Sinai Peninsula, along the Eastern Desert near modern Hurghada, and within the El Bahariya iron ores in the Western desert [21,22].

Common methods for identifying manganese (Mn) include X-ray fluorescence (XRF) and X-ray diffraction on powdered samples, as well as Raman spectroscopy and Fourier Transform Infrared (FT-IR) spectroscopy [5,6,20]. This research employs complementary non-invasive and portable analytical techniques alongside historical data to explore the use of black pigments, particularly manganese black, in ancient Egyptian artifacts. The study addresses the challenges in identifying black pigments and emphasizes the importance of maintaining a non-invasive approach. Techniques such as MA-XRF, X-Ray diffraction (XRD), and imaging in the near infrared (NIR) and short-wave infrared (SWIR) were utilized *in situ*, supported by mock-ups simulating the actual objects, to enhance our understanding of these materials.

2. Methods

In the analytical protocol for studying works of art, multiband imaging is considered the first step, as it provides reliable preliminary information about the materials, often invisible to the naked eye. Before any invasive investigation, which involves taking a sample from a specific point of the object, having an overview of the material discontinuities is essential to guide sampling in representative areas of the object, based on the analysis required.

Therefore, all the items from the tomb have been photographed in visible light (VIS) and analyzed using photographic infrared reflectography (IRR), UV-induced visible fluorescence (UVF), and visible-induced luminescence (VIL). Multi-layer Adobe Photoshop files (*.psd) were then created by overlapping the various bands (UVF, VIS, IRR, IRFC, VIL). Since each band provides specific information, the multi-layer files were used for preliminary material characterization and mapping, as well as for guiding subsequent analyses.

Following a multi-analytical approach, we combined the MA-XRF and X-ray diffraction outcomes with a multiband infrared imaging technique specifically designed to quickly and non-invasively distinguish carbon black from manganese black pigment, as described in the following sections.

2.1. The objects under investigation

In this research, we report the results obtained on three wooden polychrome caskets (Fig. 1) used as containers for the personal belongings of the deceased. A detailed description is reported in Table 1. These caskets, all dating to the same era, are crafted from wood and adorned with geometric patterns and iconographic representations following the Egyptian tradition. Of the thirteen caskets recovered in the tomb of Kha and used to store personal objects, vases made in alabaster or bed linen, only five of them show decorations, while most of them are simply white painted. The study of the painting layers documented in the funerary goods of Kha and Merit represents a significant aspect of the TT8 Project's investigation program. It includes examples from various classes of wooden and ceramic objects. Among these, the objects that exhibit the greatest complexity and pictorial richness are five wooden chests used—along with seven others painted simply white—to store personal items, alabaster vessels, and textiles [2]. During the investigations, three of these chests, sharing the same decorative and figurative repertoire, revealed the unexpected presence of manganese black, prompting further research into this specific topic. While extensive studies have been conducted on these artifacts, certain aspects, such as the workshop's organization and the painting technique employed, still remain enigmatic.

This study presents the results obtained from the analysis of three wooden polychrome caskets (Fig. 1) used to store the personal belongings of the deceased. Detailed descriptions of these caskets are provided in Table 1. These objects, dating to the same period, are crafted from wood and embellished with geometric patterns and iconographic representations characteristic of Egyptian tradition. The study of the painting layers documented in the funerary goods of Kha and Merit represents a significant aspect of the TT8 Project's investigation program. It includes examples from various classes of wooden and ceramic objects. Among these, the objects that exhibit the greatest complexity and pictorial richness are five wooden chests used—along with seven others painted simply white—to store personal items, alabaster vessels, and textiles. During the investigations, three of these chests, sharing the same decorative and figurative repertoire, revealed the unexpected presence of manganese black, prompting further research into this specific topic. Despite extensive studies on these artifacts, aspects such as the workshop organization and painting techniques employed remain unclear.

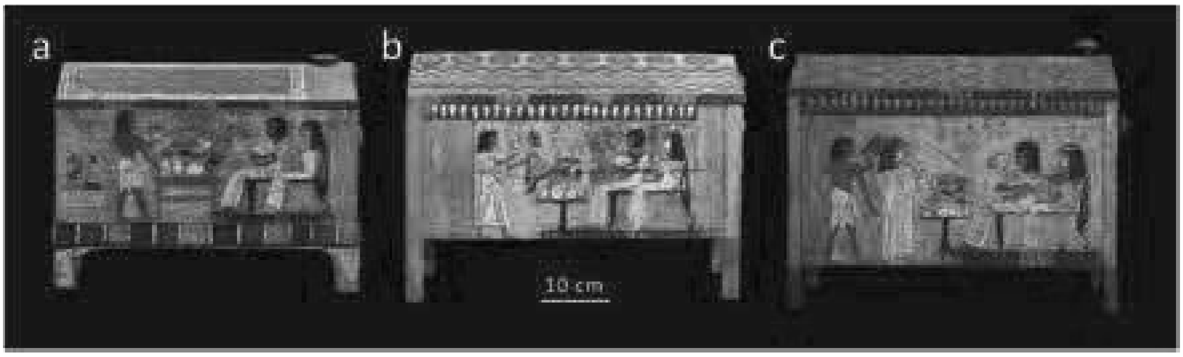

Fig. 1. The wooden caskets under investigation: a) S. 8212; b) S. 8213; c) S. 8613.

Table 1
Description of the object under investigation.

Inventory No	S. 8212 (a)	S. 8213 (b)	S. 8613 (c)
Description	Casket depicting Kha and Merit receiving offerings from one of their sons, Nakhttaneb	Casket depicting Kha and Merit receiving offerings from one of their sons, Nekhetef	Casket with an offering scene for Kha and Merit, containing loincloths and other fabrics
Dimension (cm)	44 x 30 x 34	48,5 x 35 x 36	48 x 34 x 40
Dating	1425–1353 BCE		
Material	Wood, fibers, painting	Wood, painting	Wood, painting
Period	New Kingdom		
Dynasty	18		
Kingdom	Amenhotep II/Thutmosis IV/Amenhotep III		
Provenience	Deir el-Medina/Kha tomb (TT8)		

2.2. Macroscopic X-ray fluorescence imaging

The non-destructive Macroscopic X-Ray Fluorescence imaging technique (MA-XRF) consists in scanning the entire pictorial surface of the sample using a suitably focused X-ray beam of a few hundred micrometers, generated by a primary source. During the scan, the X-ray fluorescence signals induced in the atomic species that compose the painted layers are collected point-by-point, or line-by-line if the scan is performed in continuous mode along the surface, from the acquisition system based on the use of X-ray detectors. The extension of the analysis to the entire pictorial surface through the XRF scanning technique allows to obtain the images of the chemical elements characterizing the pigments and how they are distributed on the pictorial layers [23–29].

As part of the scientific collaboration with the Institute of Cultural Heritage Sciences of the CNR (ISPC-CNR) and the Southern National Laboratories of the INFN (LNS-INFN), the wood caskets from Kha and Merit grave have been object of a wide diagnostic campaign based on the use of the advanced LANDIS-X mobile scanning system developed by the XRAYLab of Catania (Italy) [3].

The innovative real time technology of the LANDIS-X scanner allows the scanning of painted surfaces in continuous mode. The fluorescence emitted by the pictorial layers is induced by a low-power microfocus X-ray tube (30 W) with a rhodium (Rh) anode material to which a polycapillary lens is coupled. The lens allows to guide and focus the beam up to a minimum size of 50 μm (FWHM) on the sample surface for the RhKα energy at a focus distance of 14.3 mm. However, to operate the XRF imaging in macroscopic mode (MA-XRF) and precisely operating with an X-ray beam of size of 120 μm, the caskets surface was placed at a distance of 16.5 mm in order to exploit the divergence of the polycapillary lens producing a widening of the primary beam.

The LANDIS-X scanner collects the fluorescence signals emitted by the pictorial layers in event mode (TLIST mode) by employing two SDD detectors working in parallel with a spectral energy resolution of 160 eV at 5.9 keV. The two detectors are placed in 45°/45° geometry with respect to the X-ray tube, in turn positioned orthogonal to the sample surface.

The spectrometric head, in addition to the tube and detectors, is also equipped with a laser system for measuring the distance between the art object and the spectrometer in real time and eventually correcting it to maintain the same focus distance during the scan.

During the diagnostic campaign conducted at the Museo Egizio, for most of the caskets it was chosen to perform the MA-XRF analysis by scanning the entire figurative painted scene with a lateral resolution of 250 μm and a scanning speed of 25 mm/s which translates into an acquisition time per pixel of 10 ms (acquisition parameters for each casket are in Table S1). Both of these acquisition parameters have been chosen to obtain high lateral resolution elemental images that allow to appreciate even the smallest pictorial details. Finally, the X-ray source parameters have been set to 50 kV voltage and 600 μA current.

2.3. X-ray diffraction

The non-invasive X-ray diffraction (XRD) technique allows the mineralogical characterization of materials through the detection of X-rays scattered by the regular atomic structure in crystalline samples. The resulting XRD pattern is the fingerprint of the placing of atoms and thus it enables discriminating the mineralogical phases even for samples presenting the same chemical composition. To investigate the mineralogical nature of the manganese-based black pigments found on the different parts of the Egyptian caskets and previously highlighted by the MA-XRF imaging, as part of the same measurement campaign, the X-ray diffraction technique was operated *in situ* using the portable XRD system developed by the XRAYLab of the ISPC-CNR and LNS-INFN of Catania (Italy) [29,30]. The device operates XRD measurements in a parafocusing geometry. The main component of the device is a diffractometer head consisting of a microfocus Cu-anode X-ray source (50 kV max. Voltage and 600 μA max. current) coupled to a slightly focusing optic for obtaining a 186 μm size beam at a focus distance of 9.45 mm. A 600 × 1000 μm vertical slit is placed at the end of the optic and the X-ray source is 10° oriented with respect to the sample surface. During the measurement, the sample is placed at 1.5 cm out of focus distance to operate in a parafocusing Bragg – Brentano geometry. A laser system allows us to align the correct distance between the system and the sample. Primary radiation is nickel filtered to suppress Cu-kβ signal. Diffraction patterns are detected by a 1D microstrip single photon counting detector (1280 pixels, 50μm/pixel) placed at 10 cm from the sample surface and oriented at 40°. The detector covers an angular range of 16–42° 2θ collected with 0.2° angular resolution. In parallel, a SDD detector (150 eV energy resolution at Mn-Kα) collects the X-ray fluorescence signals on the same irradiated position of the sample, allowing to combine the XRD/XRF analysis. Because the beam spot size is higher than the fine Mn-based details of caskets S. 8213 and S. 8613, XRD analysis focused on S. 8212 only, where black details are broader. XRD point analysis was carried out on its hieroglyphs with dwell time of 100 s.

2.4. Infrared imaging and reflectance spectrometry

Detecting lower-mass elements like Carbon in black pigments is challenging due to the presence of various organic compounds. This research proposes an alternative method to differentiate carbon-based black materials from manganese-based black by measuring their absorbance in the Near-Infrared (NIR) and Short-Wave Infrared (SWIR) regions using spot analyses and imaging techniques. Carbon-based blacks show strong absorbance in the visible, NIR, and SWIR regions, while manganese-based black materials exhibit lower absorbance beyond 1400 nm (Fig. 2a).

The database's corresponding mock-ups (Fig. 2b) [31] validated and quantified this behavior. Mock-ups consist of wooden panels prepared using a glue-based solution (water and animal glue in a 14:1 wt ratio) applied with a brush to reduce porosity, followed by a stucco layer (gypsum added to the glue solution) and smoothing. Each rectangle hosted one pigment in six combinations of binders and varnishes. Pigment powders were ground in a mortar, mixed with a binder using a spatula, and kneaded until homogeneous. Manganese black (Kremer #47501, MnO_2 Pyrolusite) and carbon black (Kremer #26600, furnace black) were selected with a gum Arabic binder, commonly used in Ancient Egypt [1,6,19]. Measurements used Fiber Optics Reflectance Spectrometry (FORS) in the 380–2200 nm range, employing the MCS 601 UV and MCS 611 NIR 2.2 Zeiss Multi-Channel Spectrometer system, a CLH 600 tungsten halogen lamp, and 1 mm core diameter optical fibers. Acquisition geometry was $0°/2 \times 45°$ [31] with 2.5 nm spectral resolution in the NIR-SWIR range. Infrared imaging [32] in the 850–1700 nm range used a modified DSLR Nikon D810 for 850–1100 nm and an InGaAs camera (Xenics Xeva 640, cooled detector of 640x512 pixels, 12-bit) for 1000–1700 nm mounted on prototypal scanning systems [33,34]. Significant spectral differences in absorbance at wavelengths longer than 1400 nm necessitated equipping the InGaAs camera with a long-pass filter with a 1400 nm cut-off. Grey-level images were enhanced using false-color images combining Visible (Vis) and NIR/SWIR images. The green and red channels of the Vis image were shifted to the blue and green channels of the Infrared False-Color (IRFC) image, while the NIR or SWIR image occupied the red channel. In the NIR false-color image (NIR-FC), both carbon black and manganese black appeared black, while in the SWIR false-color image (SWIR-FC), carbon black remained black, and manganese black was represented in redder hues (Fig. 2b).

3. Results and discussions

Through the meticulous examination of the richly pigmented decorations on these caskets, we identified the distinct presence of manganese black. This particular pigment was selectively applied to specific areas and objects with meticulous and precise brushwork, indicating a deliberate use aimed at enhancing, refining, or correcting the artistic composition. This application required various specialized skills, reminiscent of techniques used in Renaissance workshops.

The figurative scenes on the front panels of the caskets yielded the most intriguing findings regarding materials and techniques. On casket S. 8212, the scene depicts Kha and Merit's son offering goods to his parents (Fig. 1a). The painting began with a light-yellow background layer, suggestive of the colored preparation found in panel paintings, achieved presumably by mixing orpiment, ochres and a calcium-based material (Fig. S2). Over this base layer, the profiles of the figures and objects were traced with red ochre.

The figures, objects, and decorative patterns within the scene exhibit well-defined colors. Kha and his son's skin tones were rendered using red earth, while Merit's skin tones were created with a golden yellow hue made from orpiment, an arsenic sulfide (As_2S_3) pigment derived from arsenic and originally known as "auripigmentum" literally translating to "gold paint" [35] (Fig. S3).The white clothing was realized using a calcium-based pigment (Fig. S4), applied over the skin tones to create the effect of transparency between the garments and the skin. Egyptian blue, the oldest known synthetic pigment, was used for specific objects in the offerings: some lotus flower petals, and parts of the geometric decorations. The presence of Egyptian blue, composed of the crystalline phase cuprorivaite, was highlighted by its strong response to Visible-Induced Luminescence (VIL) combined with copper mapping through the MA-XRF imaging technique and the identification of the mineral by XRD (Fig. S5).

Other offerings on the table and the lotus flower chalices likely utilized either Egyptian green (synthetic) or a copper-based mineral green (natural). These greens, similar to the blues, contain a lower amount of copper (Fig. S6) and do not exhibit VIL responses. Additionally, they both display a characteristic "dark" visible fluorescence under UV stimulation.

A black pigment is notably present in various elements of the caskets, including the hair of the three nobles, their anatomical features (pupils, eyebrows, and eye profiles), the furniture (Kha and Merit's chairs and the food cabinet), all decorative elements (dotted decorations on the lotus flowers, rectangles in the frame, and food details), and the hieroglyphs.

An underdrawing with a fine black line was discovered on the casket, where it alternated between visible sections and parts covered by pigment. Notably, a portion of this underdrawing was modified to adjust

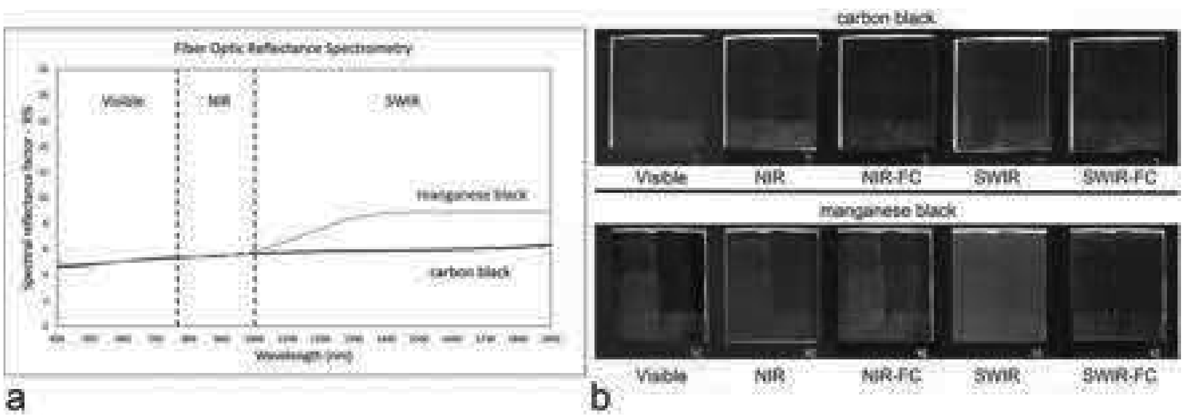

Fig. 2. a) Comparison of the spectral reflectance factors of the carbon black and manganese black showing a slight difference after 1400 nm; b) Comparison of black carbon and black manganese mock-ups in NIR and SWIR bands and the corresponding false color showing slight differences only in the SWIR band.

the position of Nakhttaneb's left shoulder in the S. 8212 casket, as illustrated in Fig. 3.

A comprehensive diagnostic campaign conducted on the burial items has revealed that some of the black areas are composed of carbon-based materials, while others were created using manganese black. Manganese black, in particular, was selectively applied to small details, specific areas, lines, or profiles that contained an abundance of intricate elements.

Fig. 4 displays the MA-XRF maps depicting the distribution of manganese on these black details, while the SWIR image confirms that the other black areas are carbon-based. A particularly interesting aspect is the thorough comparison of these two black materials within the scene to gain insights into the painting technique.

- all inscriptions, including the "full" hieroglyphs, are entirely executed using manganese black in S.8212 only, while in S. 8613 a sole hieroglyph is thickly marked with this material;
- the hair is painted with carbon-based black, and small brushstrokes of manganese black are used to delineate the contours and some curls; also, manganese black defines the outlines of the eyes, pupils, and eyebrows of Kha, Merit, and their son;
- Kha and Merit's chairs and the base on which they rest are painted with carbon black.

As previously mentioned, most elements within the scene were created in successive stages, often beginning with a red profile over which black outlines or details were later added. An in-depth examination of the food cabinet depicted in the scene on casket S. 8212 allowed for the deduction of the painting sequence, as illustrated in Fig. 5a–d. Initially, the red structure of the cabinet and the lotus flower (b) were painted, followed by the addition of details in white, yellow, red, green, and blue (c). Finally, the red and black dots were applied as the final decorative step for both elements, with additional black finishing outlines on the lotus flower (d). The elemental distribution map precisely identifies all parts made with manganese black (Fig. 5f). It is present in the black contours of the lotus flowers and the reddish outlines of the food cabinet, suggesting the use of a brush that still contained manganese black, which was then dipped in red ochre (Fig. 5e–f). A similar pattern was observed in other figures, the outlines of the offering table, and the decorations on the table within the same casket.

While blending and shading techniques are atypical in Ancient Egyptian painting, the examination of these findings suggests that the use of mixtures and combined pictorial effects was deliberate. This approach was likely intended to render shaded edges and textures, simulating genuine materials such as wood grains, by using black pigments. This indicates a sophisticated understanding of how minute quantities of black pigment could darken another pigment to achieve the desired artistic effects. Although the practice of darkening pigments is occasionally mentioned, such as with Egyptian blue [11], the scarcity of similar reports may be attributed to technological constraints, particularly in in-situ examinations. These limitations can now be overcome with state-of-the-art instrumentation capable of detecting even minute quantities of atomic elements with an atomic mass Z greater than 14.

An additional noteworthy detail in casket S. 8212 is the border of the casket lid, adorned with a geometric decorative motif that serves as a frame for the scene (Fig. 6a). This pattern, which consists of alternating small yellow and red rectangles bordered by two wide blue bands, is repeated three times. The profiles of these forms have been reworked with manganese black, although it appears the first register was overlooked (Fig. 6).

In casket S. 8213, manganese, used as a black pigment, is found in limited areas, including the top vertical lines, the borders of the white geometrical regions, and the lower part of Merit's wig (Fig. 4c–d). More broadly, manganese is prevalent in the reddish-brown decorations of the scene. Certain details reveal a specific painting technique via MA-XRF: in the pattern of the wood rings, the brush containing red ochre was successively dipped in manganese black. As a result, the top of the pattern is darker, with the blackness gradually diminishing as the brushwork progresses downward until it regains its black hue after a new dip. Manganese mixed with red ochre is also found in the profiles of the table and offerings, the lotus stem, and the lower edges of the chair. In the depiction of figures, dark red profiles were identified in the hand of Kha and Merit's son and in the wig curls of Merit (Fig. 7).

In the scene represented on casket S. 8613 (Figs. 4 and 8), manganese is used sparingly as a black pigment for a few details, appearing as corrections made by the master: a hieroglyph and the profile of Kha's son's shoulder and left thigh. Fig. 8 presents the MA-XRF correlation map of Fe, Mn, and Cu (RGB), with the details in manganese black appearing as a green false color.

In addition to mapping manganese black using MA-XRF scanning, optical techniques were applied to achieve similar results reliably. The use of the Short-Wave Infrared (SWIR) band after 1400 nm allowed us to select a range where carbon and manganese black exhibit differences in reflectance. Fig. 9 illustrates the comparison between MA-XRF (Fig. 9b) and SWIR-FC (Fig. 9c), where the white areas of the Mn map correspond to the reddish hue in the false-color image. These small areas, such as those in the hair curls, can be further distinguished from the larger and darker areas of the hair, which were realized using carbon black. The same distinction applies to the lotus flower on the right of the detail.

Another noteworthy detail observed in SWIR-FC is the depiction of hieroglyphs in Fig. 10, again corresponding to casket S. 8212. In this detail, the ink used for rendering the characters was manganese-based, characterized by a reddish hue (Fig. 10a) that precisely corresponds to the distribution of Mn obtained through MA-XRF (Fig. 10b). The distinctive feature of this manganese-based ink can be differentiated from carbon-based elements, as indicated by the two white arrows in Fig. 10a, representing areas that remain black even in SWIR-FC. The blue arrow, on the other hand, indicates the presence of a Mn-rich area that does not correspond to any of the dark-colored visible pictorial

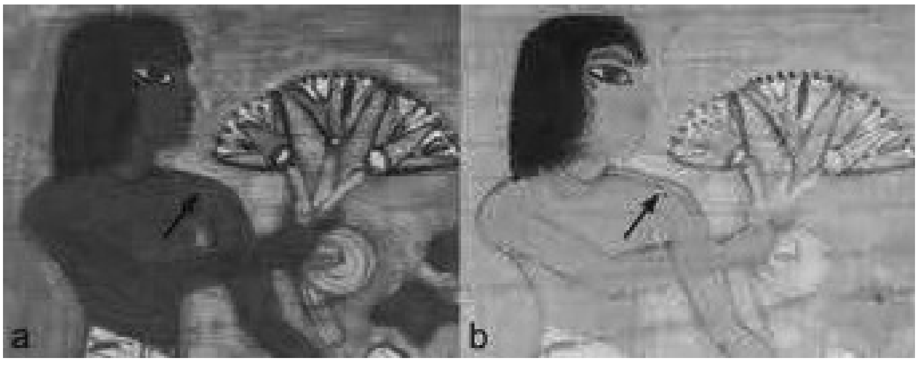

Fig. 3. Detail of the S. 8212 casket in: a) Visible; b) SWIR, showing the modified line of the shoulder, as indicated by the arrow.

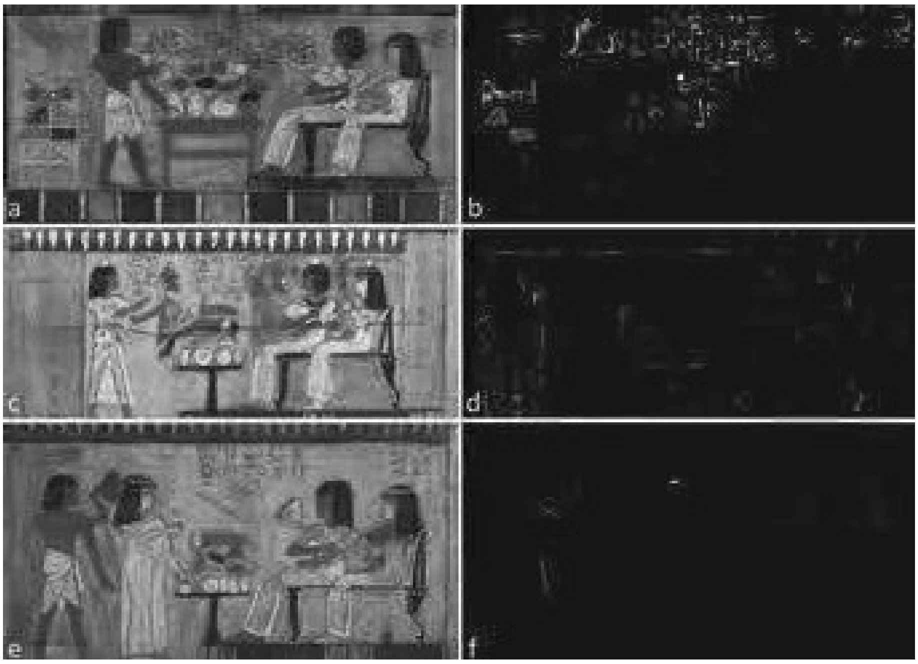

Fig. 4. Comparison of the Visible image of the three caskets (a: S.8212; c: S.8213; e: S.8613) and the corresponding detail (b, d, f) where white areas show the distribution manganese acquired by MA-XRF.

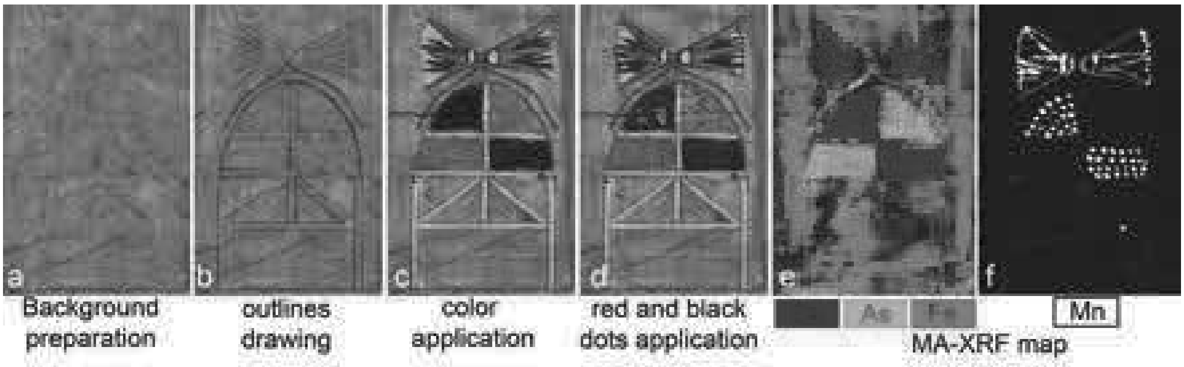

Fig. 5. Detail of the food cabinet of casket S. 8212, simulation of the scene realization steps: from the prepared wood (a) to the outlines of the structure and the lotus flower in red ochre (b); the white, blue, and red spots (c); the red and black dots applied as last decoration step on top. MA-XRF correlation map of Fe, As, Cu given as an RGB false color image (e); MA-XRF map of Mn (f).

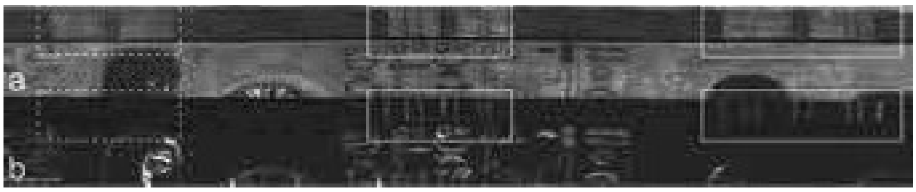

Fig. 6. Detail of the border of the lid in the S. 8212 casket where the geometrical pattern frames the scene and the first register lacks? manganese black lines in the XRF grey map of manganese.

elements. In fact, this area has been later covered with an arsenic-based pigment, probably the same used for the background (Fig. 10c) This is consistent with an artistic process that shows slight variations, as already mentioned for other areas of the casket, such as the detail of Fig. 3.

In the hieroglyphs of casket S. 8212 (Fig. 11b), where the presence of manganese black is abundant, the combination of XRF and XRD has identified distinctive compositional features of this pigment. The predominant mineral is manganite, with traces of pyrolusite (Fig. 11c). This result contradicts the generally accepted composition of manganese black, typically described as mainly or solely composed of pyrolusite. At the same time, this finding restricts the potential sources for the manganese black used on this casket. Of the known Egyptian manganese ores, manganite is abundantly present at Gebel Abu Shaar in the Eastern Desert and in the Um Bogma region of Sinai [22]. Although both sites have been known for their dominant copper mining industry since the Middle Kingdom [36,37], compositional evidence from the present XRF investigation—specifically the presence of Ba (Fig. 11a and Fig. S7)

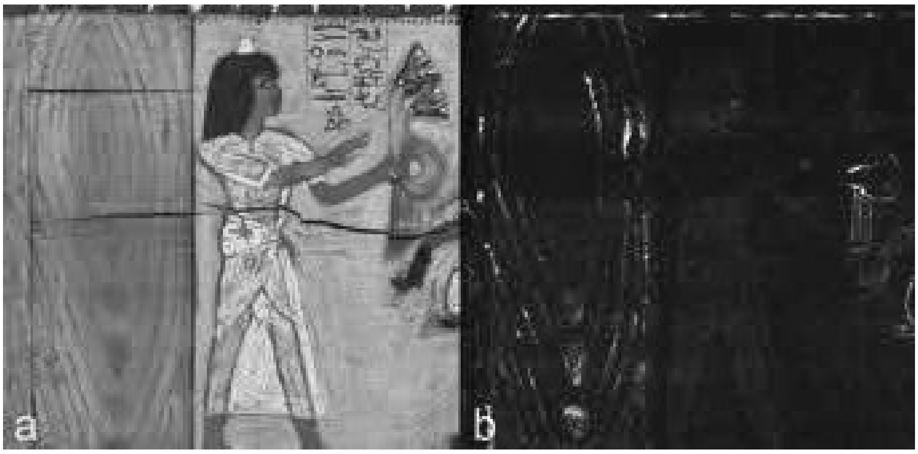

Fig. 7. Casket S. 8213, detail of the son Nekhetef in visible (a) and XRF map of manganese (b).

Fig. 8. Casket S.8613; XRF map of Fe, Mn and Cu as RGB false color image.

Fig. 9. Casket S.8212; detail of the face of the son Nakhttaneb in visible (a), XRF map of Mn (b) and SWIR false color image (c).

supports the hypothesis that the manganese black on the casket originates from the Eastern Desert, where barite is described as an associated mineral.

Gebel Abu Shaar, located between modern Hurghada and El Qoseir in the ancient Wadi Hammamat mining region east of Coptos, is geographically proximate to Deir el-Medina, providing further evidence for its exploitation in the New Kingdom. Finally, the varieties of manganite in the Sinai and the Eastern Desert differ, with the latter described as very fine, with a darker grey color and brownish tint [17], characteristics that might fit its use for the fine details and brownish hieroglyphs on the caskets.

4. Conclusions

The presence of manganese black on three wooden polychrome caskets from the tomb of Kha and Merit was detected using MA-XRF. Preliminary results showed that the presence of manganese on these caskets appears to correspond to very fine details, as a final step to complete the profiles made with carbon black. This result and the unexpected presence of manganese together with carbon black was our starting point for this investigation.

In addition to the MA-XRF analysis conducted using a rapid and innovative scanning system, we have developed an infrared imaging acquisition method that is suitable for discriminating black pigments

Fig. 10. Casket S.8212; detail of the hieroglyphs in SWIR false color image (a) XRF map of Mn (b) and Mn/As (Red/Green) correlation map highlighting that the black detail, based on manganese black and faintly visible to the naked eye, was covered with an arsenic-based layer of light color in the final step of the realization (blue arrow). White arrows indicate carbon-black areas that remain black in SWIR-FC in contrast to the reddish areas realized with manganese black.

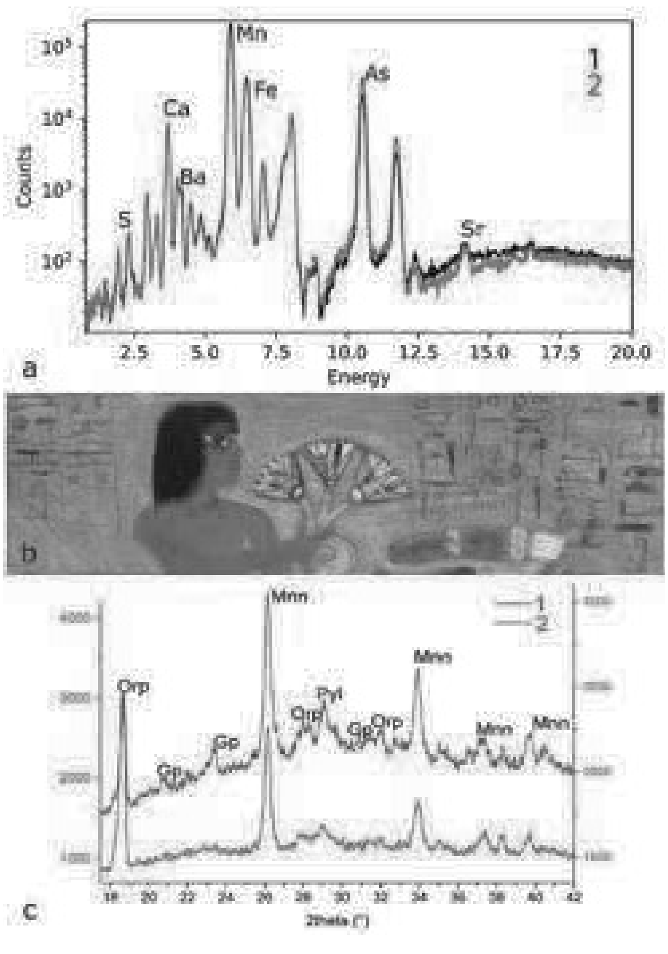

Fig. 11. Casket S.8212; detail of the left and right hieroglyphs with XRF (a) and XRD (c) data from point analysis (b). Mineral abbreviations in (c) are according to IMA–CNMNC: gypsum = gp, manganite = mnn, orpiment = orp, pyrolusite = pyl.

and can be performed in a time frame comparable to that of a photograph. This method relies on the spectral distinctions between manganese black and carbon black in the Short-Wave Infrared (SWIR) region, which is most pronounced in the 1400–1700 nm range. To achieve this, we filtered an InGaAs camera with a 1400 nm interferential long-pass filter, allowing us to acquire infrared images of the artifacts. This method was successfully tested on mock-ups, displaying a red false color for manganese black. With this approach, it becomes possible to differentiate between carbon and manganese black, thus bridging the gap in the detection of light elements by XRF spectroscopic techniques. To the best of our knowledge, various forms of carbon black were commonly known in ancient Egypt, whereas very few references have reported the use of manganese black. Confronted with the compelling evidence of our results and recognizing the existing analytical limitations in identifying black pigments, we posit that the use of manganese-based blacks may have been more widespread than previously documented in the literature.

There are very few sources that report the use of manganese black in Ancient Egypt, and there is no information on the execution technique associated with the use of this pigment. Given the results, we hypothesize that the use of manganese black may have been more widespread than previously reported in the literature.

The use of carbon black and manganese black in the painted box S. 8212, which is currently unique in the Egyptian material evidence, undoubtedly opens up a fascinating and novel avenue for investigating the organization of craftsmanship in ancient Egypt. The presence of traces of manganese black in the other two twin caskets, which were probably made by a different craftsman or by the same craftsman at different times, shows that artisans brought personal skills, execution practices and techniques from time to time within a homogeneous project such as the production of a few objects for funerary offerings.

The organization of artisanal work in ancient Egypt, particularly in areas like Deir el-Medina, was characterized by an extremely flexible and dynamic management of commissions. Artisans in these regions often worked simultaneously on state and private projects [38], which forced them to adapt their techniques and styles to the different requirements. In this context, the casket that shows the most consistent use of manganese black probably represents an artisan who incorporated this technique into private works, possibly reflecting undocumented practices that were common in larger pictorial projects such as tomb decorations [11]. For large-scale projects, practical considerations in material selection and technical approaches were paramount. The use of manganese black, with its relatively short preparation time, would have been advantageous for large-scale painting projects where efficiency was crucial. While manganese black was not ideal for covering large areas, it excelled at tracing fine lines and intricate detail, making it particularly valuable for decorative applications that required precision.

To further explore this hypothesis, a comprehensive mapping of the artifacts is currently underway, using a combination of appropriate and multidisciplinary analyses.

Once we have collected data on several artifacts, we intend to map the use of manganese black, considering both the technical aspects of the material and the symbolic meaning of its use. This could include the accentuation of decorative elements with symbolic functions or the reworking of hieroglyphs by the hand of a more experienced artist.

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CRediT authorship contribution statement

Tiziana Cavaleri: Writing – review & editing, Writing – original draft, Visualization, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Paola Buscaglia:** Writing – original draft, Formal analysis, Data curation. **Enrico Ferraris:** Validation, Resources, Investigation, Formal analysis. **Marco Gargano:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Michela Botticelli:** Writing – review & editing, Validation, Formal analysis, Data curation. **Francesco Paolo Romano:** Writing – review & editing, Supervision, Resources, Investigation, Formal analysis, Data curation. **Claudia Caliri:** Writing – review & editing, Visualization, Supervision, Resources, Investigation, Formal analysis, Data curation.

Declaration of competing interest

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Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2024.112400.

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