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Keywords: Boğazköy, Pigment, Portable X-ray Fluorescence Analysis, Roman Wall Painting, Painted Plaster – *Schlagwörter:* Boğazköy, Pigment, Portable Röntgenfluoreszenzanalyse, Römische Wandmalerei, Bemalter Putz – *Anabtar sözcükler:* Boğazköy, Pigment, Taşınabilir X-Ray Floresan Cihazı ile Analiz, Roma Duvar Sanatı, Boyalı Siva

INTRODUCTION

In 2014 the initial traces of a building were uncovered near the rock outcropping referred to as the Mihraplıkaya in the lower city area of Boğazköy-Hattuša. In 2015, further excavation revealed a building that is characterized by a supply of water coming through multiple water channels draining into several basins. The building is estimated to be at least 18 meters across and directly connected to a niche in the rock outcropping. The function of the building is still unknown, as parallels are difficult to find. However, a 2nd century A.D. date is suggested by comparison with stylistic elements found in the detritus of Hanghaus 2 at Ephesus¹. A coin from the later reign of Valentinian (ca. 367–375) suggests a long use for the building, though the coin's findspot suggests caution. The building in Hattuša included walls that were decorated with painted plaster. The focus of this study is to report initial characterization of the pigment profiles in the painted plaster through portable X-Ray Floresence (pXRF) analysis to aid in decisions about preservation.

ARCHAEOLOGICAL PROVENANCE AND SAMPLES

The original location of the wall paintings is unknown. They were recovered from a rectangular section of the smaller basin into which a mixture of painted and unpainted plaster and some mosaic fragments fell, in the southeast portion of the excavation area. It is possible that they fell down from a terrace above the basins. Reconstruction of some portions of the wall paintings

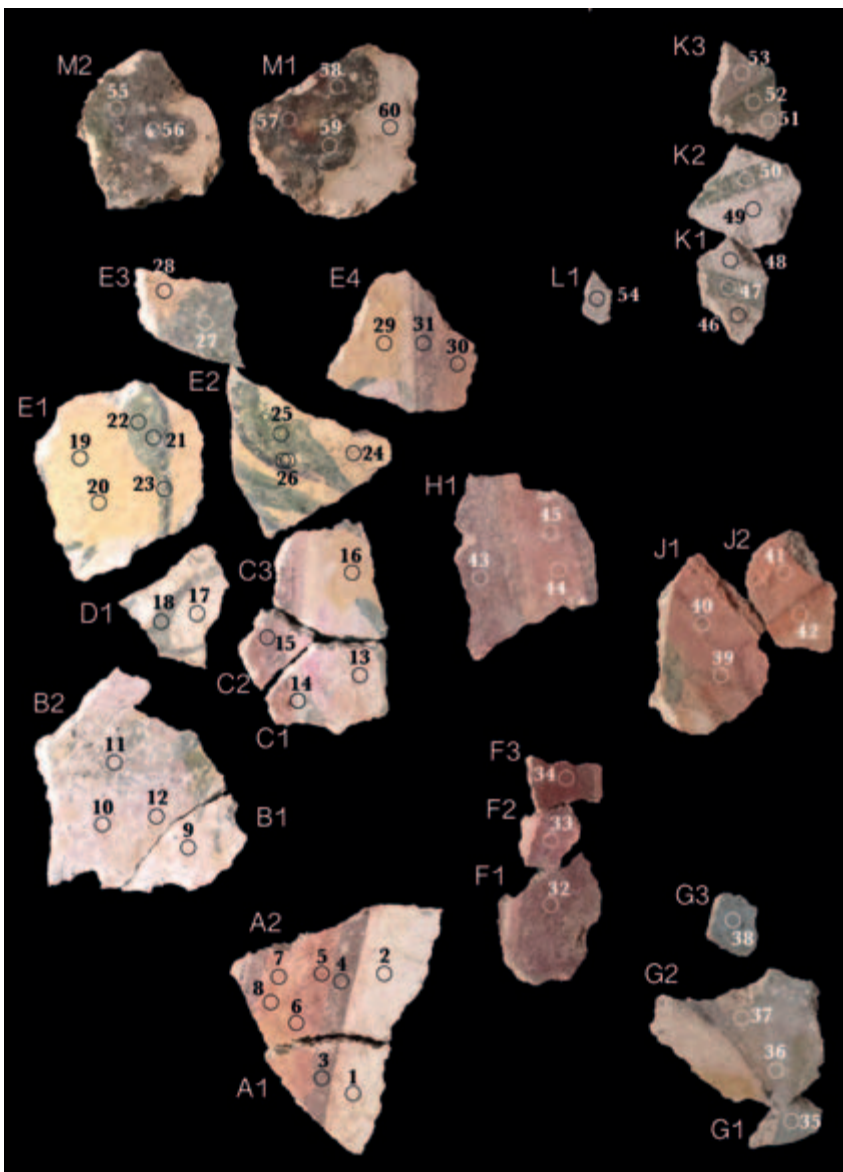
Sources of illustrations: Figs. 1–18 = Author.

¹ Krinzinger 2002.

Fragment	Scan	Pigment Profile	Fragment	Scan	Pigment Profile
A1	1	White	J1	39	Red
A2	2	White	J1	40	Red
A1	3	Red	J2	41	Red
A2	4	Red	J2	42	Red
A2	5	Red	H1	43	Red
A2	6	Red	H1	44	Red
A2	7	Orange	H1	45	Red
A2	8	Orange	K1	46	White
B1	9	White	K1	47	Green
B2	10	Green	K1	48	White
B2	11	Green	K2	49	White
B2	12	Green	K2	50	Green
C1	13	Yellow ochre	K3	51	White
C1	14	Pink	K3	52	Green
C2	15	Bright Yellow	K3	53	White
C3	16	Yellow ochre	L1	54	Green
D1	17	White	M2	55	Dark organic brown(?)
D1	18	Green	M2	56	Dark organic brown(?)
E1	19	Yellow ochre	M1	57	Dark organic brown(?)
E1	20	Yellow ochre	M1	58	Dark organic brown(?)
E1	21	Green	M1	59	Dark organic brown(?)
E1	22	Green	M1	60	White
E1	23	Green	N1	61	Orange
E2	24	Yellow ochre	N1	62	Orange
E2	25	Green	N2	63	Orange
E2	26	Green	N2	64	Rose/Pink
E3	27	Green	N3	65	Orange
E3	28	Yellow ochre	N3	66	Rose/Pink
E4	29	Yellow ochre	O1	67	White
E4	30	Bright yellow	O1	68	White
E4	31	Red	O1	69	Bright yellow
F1	32	Burnt ochre	O2	70	Bright yellow
F2	33	Burnt ochre	O2	71	White
F3	34	Burnt ochre	O3	72	Bright yellow
G1	35	Blue-Green	P1	73	Dark organic brown(?)
G2	36	Blue-Green	P1	74	Dark organic brown(?)
G2	37	Blue-Green	P1	75	Dark organic brown(?)
G3	38	Blue-Green			

Table 1 Identification of fragments and scan locations with visual identification of color as displayed in Figures 1–3

Fig. 1
Plaster fragments
A1–M2 with scans
1–60



show that there were different decorative patterns and scenes, some with floral elements, enclosed in painted framed panels. The pieces examined for this study were drawn from portions of the wall paintings that display similar patterns as those published previously².

The pieces analyzed were selected to provide a sample of as many different pigment effects as possible. Table 1 provides an overview of the fragments and scan locations pictured in *Figures 1–3*. The frescos were painted over dried plaster as suggested by the detectable binders, and the degree to which lead-intensive pigments shield the signature of the base plaster. A number

² Schachner 2016, 12–19. In particular note figs. 31–33.

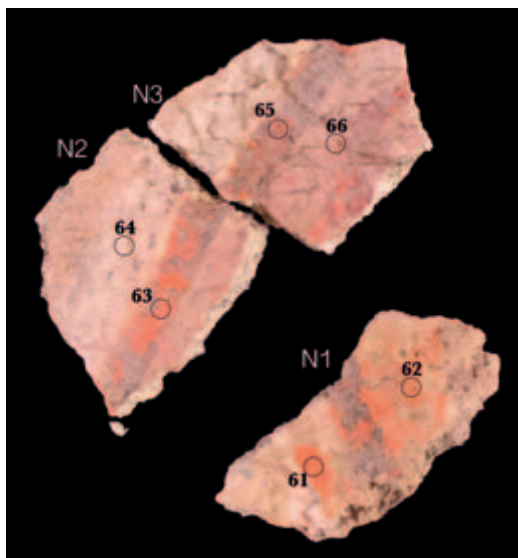


Fig. 2 Plaster fragments N1 – N3 with scans 61–66



Fig. 3 Plaster fragments O1 – P1 with scans 67–75

of artistic elements were clearly identifiable. The figuration of foliage on light background can be seen in pieces D1, E1, E2 and E3, and possibly also in K1, K2, K3. The depiction on M1 and M2 is more difficult to interpret. It could be a sort of flower, but this is far from certain. However, this may have some relation to the pigmentation used there. In several other places, the figuration is more geometric (A1, A2, G1, G2, G3, H1, N1, N2, N3, O1, O2, O3). In other cases, the relation between the effect the artist or craftsman was trying to render and the choice of pigmentation is not always clear.

INSTRUMENT AND SETTINGS

The instrument used was a Bruker Tracer IV SD portable energy dispersive XRF instrument (Serial # T4S1130). The instrument was controlled from a laptop using Bruker proprietary software for instrument settings adjustment (X-Ray Ops v1.2.21) and assay capture and naming (S1 PXRF version 3.8.30). Beam conditions for this study were 45 KeV and 30 mA with a 25 μm Ti 300 μm Al filter (Yellow) and 90 second assay time. The multi-channel analyses of the instrument has 1024 channel configuration with an area of measurement of 7 mm^2 , though the area of measurement is focused within a smaller concentration of around 3 mm^2 area. For this study, the objects presented for analysis were photographed and labeled according to the approximate location of the pXRF scan. The instrument did not have a camera to aid in precise positioning while on the instrument, so an error of 2–3 mm was possible in relation to the labeling and the actual scan. See, for example, the results from scan 71.

Within the analyzed fragments, there were ten pigment profiles differentiated. Underneath the various pigments always lay 1) the white plaster base, which could be brightened

with the addition of some lead. Beyond the pigment profile provided by the plaster, we propose the presence of nine more pigment profiles: 2) yellow ochre, 3) bright yellow, 4) orange, 5) rose/pink, 6) red, 7) green, 8) blue-green, 9) burnt ochre brown, and 10) dark organic brown. Discussion of each pigment profile follows below. Of the nine pigment profiles, two were identified as likely organic-based (green, and the ›dark organic brown‹) aiding in decisions on how to proceed with preservation. In most cases, the pigment profiles reflect the expected palette for Roman frescoes of the period. A few uncertainties may be resolved by further analysis by different methods. First, the analysis of bright yellow also leaves the possibility of trace amounts of lead chromite, which is unexpected. Second, the original color of the pigment profile ›dark organic brown‹ remains unsure. It is likely changed from its original color either by contact with the fill during its time in the ground, or simply over time.

LIMITS AND INTERPRETATION OF ANALYSIS

Portable X-Ray Fluorescence analysis has its advantages and limits³. XRF analysis has long been recognized as a non-destructive way to analyze pigment⁴. However, elemental characterization cannot always establish particular compounds, and is best used in combination with other methods⁵. Elements of lower atomic weight displace electrons at low enough energies that they will not sufficiently escape the object of analysis or travel through the air between the object of analysis and the detector to be recognized. Thus elements lighter than titanium cannot be measured consistently, though the presence of elements down to magnesium can be detected⁶. Moreover, to calibrate the relative concentrations of the material analyzed, the appropriate settings on the instrument must be used to fit the material being analyzed, and compared with known samples. In the present case the instrument was calibrated for use on clay tablets. While these settings were sufficiently useful for the present analysis, the combination of known reference samples, and appropriate settings were not available on site. Thus the present analysis is qualitative, relying on the raw spectrum provided by the instrument.

Using the raw spectra requires interpretation, but also provides useful comparative data for comparing the pigments and the pigment carriers. Interpretation involves a consideration of the combination of elements present in the locations scanned, their relative density and concentration, and other factors⁷. For example, in areas with darker red pigmentation, a high use of lead affects the detection of the high calcium carbonate plaster⁸. Pigments as powders were used to make the paints, but before application it is not sufficient to simply add water. A binder or carrier paste must be used, preferably something which will not affect the color of the pigment. Traditionally Roman painters used a calcium carbonate paste, made from powdered eggshells, mollusk shells, chalk or marble. This accounts for the high calcium reading obtained in virtually all the spectra taken from painted areas. In addition, the plaster on which the paintings

³ Speakman et al. 2011; Frahm – Doonan 2013.

⁴ Szökefalvi-Nagy et al. 2004; Shugar – Mass 2012.

⁵ Janssen et al. 2013.

⁶ Hunt – Speakman 2015.

⁷ Hunt – Speakman 2015.

⁸ See the section on reds below.

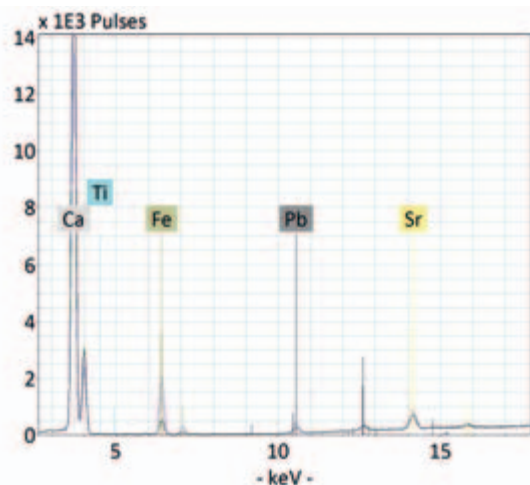


Fig. 4 Spectra of base plaster (basic) white scans 1. 2. 9. 17

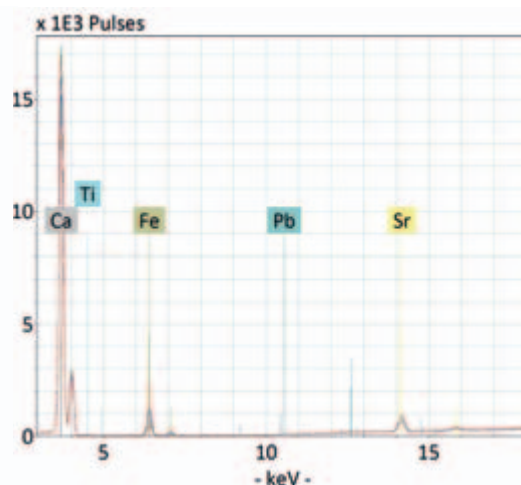


Fig. 5 Spectra of base plaster (basic) white scans 46. 48. 49. 51. 53. 60

were executed would have been lime based, also accounting for high Ca values on the unpainted areas. Completely separating a characterization of the elemental content of the substrate (the plaster) from the paint is therefore not an easy matter based on spectra alone. Therefore in this case we deal mainly with the elements we believe to make up the pigments, and make no firm identification of the substrate layer.

These observations are considered preliminary. Though in most cases the designations are clear, some aspects of the material of the pigment will not be detected by the pXRF and therefore cannot be validated with certainty. We can identify the elements. However, without optical analysis, determining the exact mineral from which the pigment is formed remains to be confirmed. In this instance reference to proposed mineral sources has been made using several works on Roman painting⁹.

DISCUSSION OF INDIVIDUAL PIGMENTS

White

(Basic) White

We interpret this signature to represent most clearly the base plaster (scans 1. 2. 9. 17 in *fig. 4*; scans 46. 48. 49. 51. 53. 60 in *fig. 5*). There is a high Ca (calcium) content, the PbO (lead oxide, massicot) might have been used as an ingredient in a surface wash to make a brighter white (but we would expect more, in such a case).

(Brightened?) white

This sub group was characterized by the brightness of the white observable during selection (scan 67 blue, 68 green, 71 red in *fig. 6*). But it is not substantively different in composition from

⁹ Wornum 1841; Siddall 2006; Eastaugh et al. 2008; Piovesan et al. 2011.

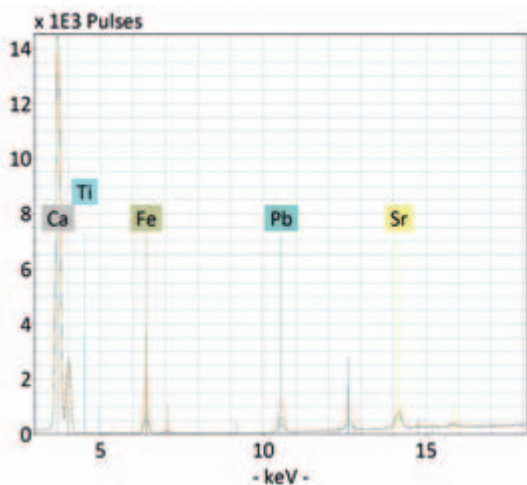


Fig. 6 Spectra of (brightened?) white pigment scans 67 (blue spectrum), 68 (green spectrum), 71 (red spectrum)

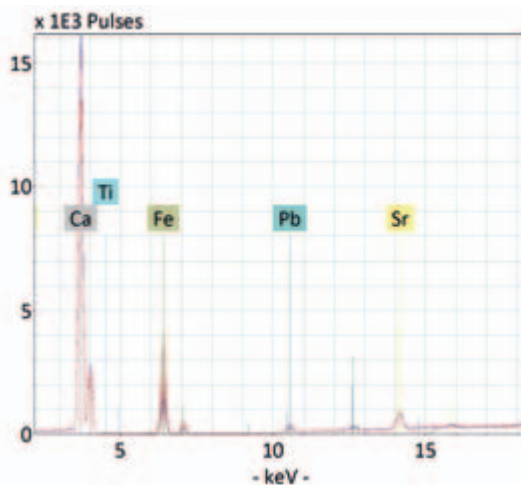


Fig. 7 Spectra of yellow ochre pigment scans 13. 16. 19. 20. 24. 28. 29

the white plaster. The higher detection of lead in 71 may be due to an overlap of analysis with the proximal yellow pigment or dilution/migration of the yellow pigment.

Yellow ochre

This pigment profile appears to be a diluted yellow ochre [limonite-hydrated iron oxide- $\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$] as visible in the spectra (scans 13. 16. 19. 20. 24. 28. 29 in *fig. 7*). By diluted, we mean that only a small amount of the color pigment was used in a larger quantity of calcium (Ca) based carrier. The much lower lead (Pb) content in this yellow distinguishes it from the bright yellow.

Bright yellow

The yellow stripe on fragments O1, O2, O3 (scans 69. 70. 72) exhibits high levels of lead (Pb), and some strontium (Sr) (scans 30. 69. 70. 72 in *fig. 8*)¹⁰. There is also a detectable level of tin (Sn) in scan 30 (*fig. 9*)¹¹. The high level of Pb, and possibly the thickness of the paint account for the weaker detection of calcium (Ca). The high level of Pb also suggests the lead oxide masticot (PbO). Two other characteristics of the pXRF assay are notable. It is possible to interpret

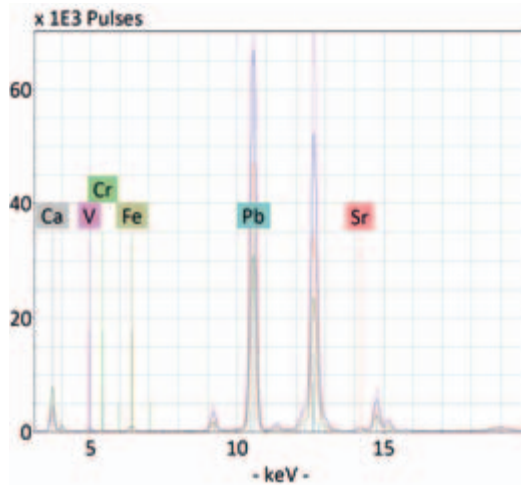


Fig. 8 Spectra of yellow stripe pigment scans 30. 69. 70. 72

¹⁰ The slight peak on the right side of the figure is from Rhodium. This pXRF machine produces radiation by exciting Rhodium with high voltage. This peak is also visible in Figures 10. 12. 15–17 and 18.

¹¹ The three Rhodium peaks between 19 and 21.5 keV here, and found in Figures 11 and 14, are not indicative of the pigment composition.

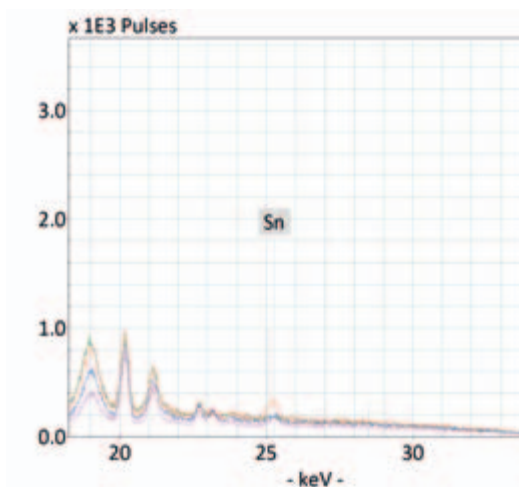


Fig. 9 Spectra of yellow stripe pigment scans 30. 69. 70. 72 – focused on detection of tin

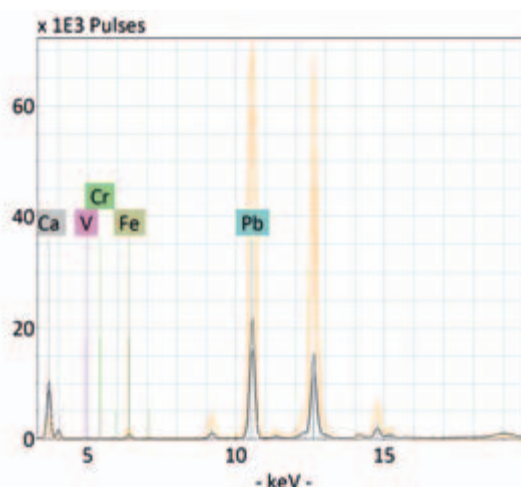


Fig. 10 Spectra of (bright) orange pigment scans 7. 8 (black spectra); 61–63. 65 (orange spectra)

the spectra to indicate the presence of both chromium (Cr) and cadmium (Cd). Different pigments could be used in combination, and the further trace elements could be interpreted as supplementary pigments. However both interpretations are doubtful. The peak labeled as Cr in the figure is likely produced by vanadium (V). The presence of lead chromite (PbCrO_4) is doubted as it tends to discolor quickly in the presence of air. It is possible that its combination with the massicot or some other undetectable organic compound could have protected it. It is also possible to interpret the presence of cadmium yellow (CdS) in the pigment profile. Roman technology is not known to have used CdS , generally precipitated out of widely available zinc ore sphalerite, or the occasionally co-occurring wurtzite. However, the peak to the right of Sr should be interpreted as Pb rather than Cd. Unexpected Naples yellow [$\text{Pb}(\text{SbO}_3)_2/\text{Pb}_3(\text{SbO}_4)_2$] is ruled out by the lack of antimony (Sb).

Orange

(Bright) orange

This appears to be some form of lead-chromium pigment [crocoite (PbCrO_4)?] (scans 61–63. 65, colored orange in *fig. 10*). The Cr peak is very small on the spectra, but this data is uncalibrated, so it is possible that the Pb is drowning it out. The peak to the left of Pb may include gallium (Ga, not labeled), which is sometimes present alongside Pb. There is also a strong presence of tin (Sn) (*fig. 11*).

(Pale) orange

This is a diluted use of the same pigment as the (bright) orange (scans 7. 8, rendered in black in *fig. 10. 11*). Very similar spectra, but with lower levels of all the characteristic elements. However, there is a higher level of vanadium (Va) exhibited than in red pigments (*fig. 10*).

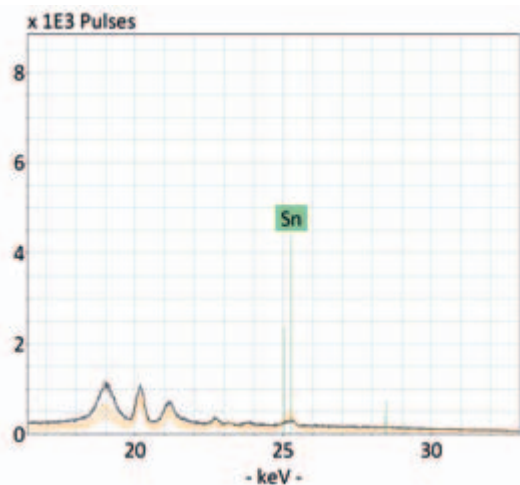


Fig. 11 Spectra of (bright) orange pigment scans 7. 8 (black spectra); 61–63. 65 (orange spectra) – focused on the detection of tin

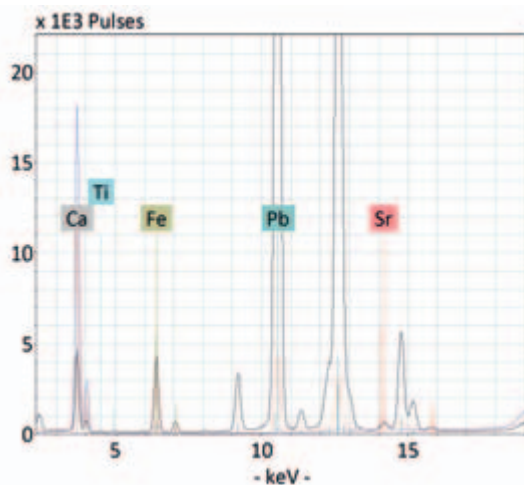


Fig. 12 Spectra of base plaster, pale pink, and pale rose pigment scans 1 (base plaster, blue spectrum), 64 (pale pink, red spectrum), 66 (pale rose, black spectrum)

Rose/Pink

Pale Pink

This pigment is high in lead (Pb) (scan 64, *fig. 12*). It also has higher than normal iron (Fe) content. The spectrum for scan 1 (white, spectrum colored blue) is included in the figure for comparison.

Pale Rose

This pigment has a much higher lead (Pb) and iron (Fe) than ›Pale Pink‹ (scan 64) but may be a less diluted form of the same pigment (scan 66, colored black, *fig. 12*).

Red

All reds appear to be stronger or more diluted forms of lead oxide (Pb_3O_4) (*fig. 13*). Tin (Sn) is also present in all of the scans (*fig. 14*). These

different shades can be broken down into three concentrations, weakest to strongest:

Paler Red

These have small enough lead (Pb) concentrations that the calcium (Ca) from the plaster is still detected (scans 3–6, rendered in red on *fig. 13*). Scan 14 (rendered in yellow in *fig. 13*) also belongs to this group, though the levels of lead are higher.

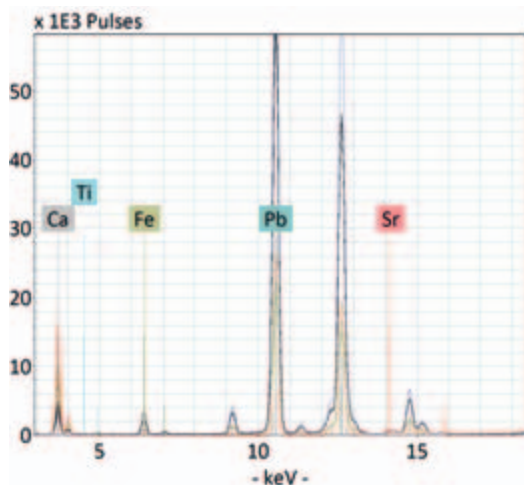


Fig. 13 Spectra of red pigment scans 3–6 (paler red, red spectra); 14 (paler red, yellow spectrum); 31. 44. 45 (medium red, green spectra); 39. 40–42 (darker red, black spectra)

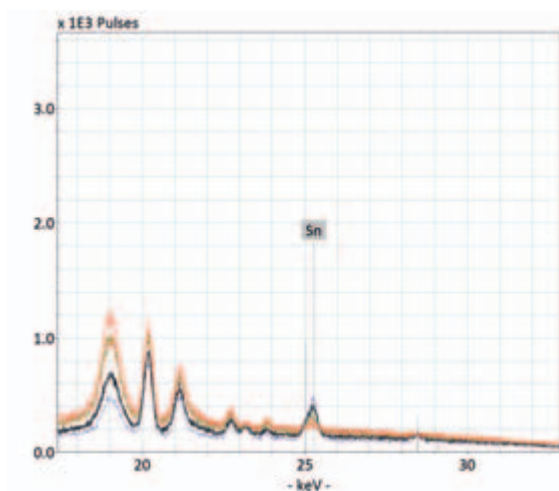


Fig. 14 Spectra of red pigment scans 3–6 (paler red, red spectra); 14 (paler red, yellow spectrum); 31. 44. 45 (medium red, green spectra); 39–42 (darker red, black spectra) – focused on the detection of tin

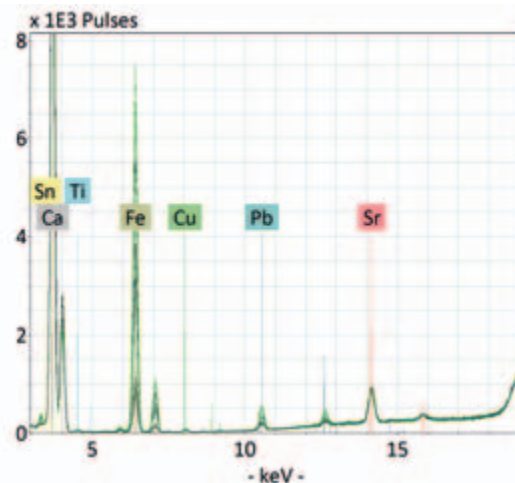


Fig. 15 Spectra of green pigment scans 11. 12. 22. 25. 27. 47. 50. 52. 54 (green, green spectra); 18. 23. 26. 73–75 (darker green, black spectra); 10, 12 (lighter green, light green spectra)

Medium Red

Higher levels of lead and corresponding lower level of calcium (Ca) distinguish this group as a less diluted mixture than ›paler red‹ (scans 31. 44. 45 rendered in green in *fig. 14*).

Darker Red

This group, even less diluted, had the highest amount of lead (Pb), and the lowest signature of calcium (Ca, scans 39–41, rendered in black in *fig. 13*). Scan 42 represents an even less diluted, and hence brighter mixture of the pigment profile (black in *fig. 13*).

Green

The lack of significant peaks for any elements other than those expected for the base plaster suggests that the principal pigment is carbon-based (scans 11. 21. 22. 25. 27. 47. 50. 52. 54, *fig. 15*). This also applies to the darker shades of green present in depiction of foliage (scans 18. 23. 26. 73–75, *fig. 15*). All greens share concentrations of iron (Fe), and small amounts of lead alongside Sr (*fig. 15*). However, the absence of any element in significant quantity from which the expected group of oxide/carbonate/sulphate pigment compounds seems to suggest that whatever is producing the green color is organic. Iron-rich glauconite or celadonite (green mineral pigments) is unlikely. Both include aluminium (Al) as a major constituent, and none is detected¹². Lighter greens (scans 10, 12) are distinguished from darker greens by higher concentrations of Fe. A very small amount of copper is detectable in the scans.

¹² Aluminum (Al) is poorly measured by pXRF, but its presence is detectable.

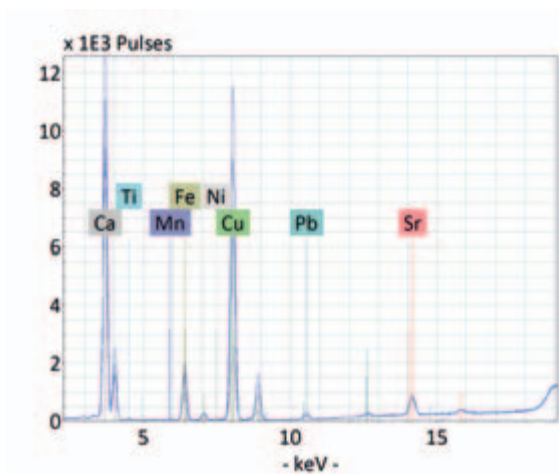


Fig. 16 Spectra of blue-green pigment scans 35–38

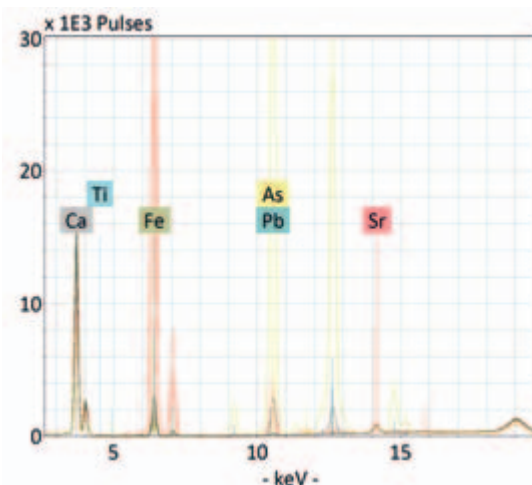


Fig. 17 Spectra of yellow ochre, burnt ochre, and dark organic brown pigment scans 15, 30 (yellow ochre, yellow spectrum); 32–34 (burnt ochre, red spectra); 55–59 (dark organic brown, brown spectra)

Blue-Green

The high signature for copper (Cu), lead (Pb) and strontium (Sr) suggest one of the blue-greens traditionally rendered with copper (Cu) compounds, verdigris of various types (copper oxides carbonates) and copper sulphates (scans 35–38, *fig. 16*). Trace amounts of titanium (Ti), and manganese (Mn). The presence of iron (Fe) is something for which we cannot provide a good explanation.

Burnt ochre

The primary pigment compound seems to be a burnt ochre iron oxide [$\text{FeO}(\text{OH})$] inferred from the predominance of iron (Fe, scans 32–34, the red spectra in *fig. 17*). Sienna is excluded by the lack of manganese (Mn). Lead (Pb) is present but only in a small amount. Arsenic (As) is also present. The main L energy level of As overlaps with the main K energy level of Pb, but one of the As peaks is distinct¹³. For comparison, yellow ochres (scans 15, 30) are included in the figure as yellow spectra.

¹³ K, L, M, (and N, O, P) are labels assigned to electron energy levels in any atom. The K shell holds up to 2 electrons, and is the smallest shell around the nucleus. Next out, the L shell can hold 8 electrons, and the M shell 16 electrons. When radiation hits an atom and displaces an electron in an inner shell, an electron from an outer shell will fall into the lower shell and release a photon. Electrons that fall into the K shell release an electron of a lower energy than electrons that falls into the L shell. The respective K and L energies for each element are different for each element, and increase in relation to the atomic weight. In this case, an electron falling to the K level in a heavier Pb (lead) atom releases about the same energy that an electron falling into the L shell in lighter As (arsenic).

Dark organic brown (?)

A different pigment profile is revealed in distinction to burnt ochre, though it also appears brown. The rendition of flowers suggests that the original color was not what it appears now (scans 55–59, rendered in brown on *fig. 17*). Comparison with scan 13 (yellow ochre pigment), with clear identification of calcium (Ca), combined with little evidence of any heavy elements suggests an organic pigment. If the present material preserves the original color, a sepia pigment, such as from squid ink, is possible, *fig. 18* shows scan 57 (spectrum colored blue) as an outlier from scans 55. 56. 58. 59 (spectra colored dark brown) with some lead (Pb). We interpret this as a red layer underneath.

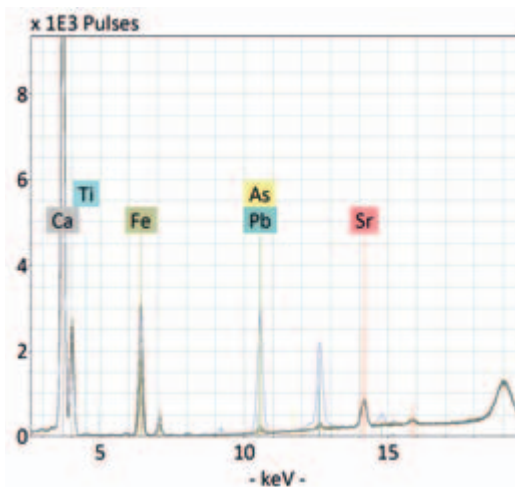


Fig. 18 Spectra of dark organic brown pigment scans 55. 56. 58. 59 (brown spectra); 57 (blue spectrum)

CONCLUSION

It is possible to use pXRF for initial characterization of material composition of pigments in the field. In the present study, it was possible to distinguish a range of different pigment profiles, allowing for decisions to be made about preservation processes. The method is clearly useful because it is non-destructive, and is superior to other processes¹⁴. The limitations of characterization are also clear. While the likelihood of an organic source of pigmentation is suggested by the lack of likely mineral pigmentation, a more secure characterization is beyond the detection limits of the instrument. Nonetheless, the painted plaster fragments recovered from the basins adjacent to Mihraplikaya at Boğazköy-Hattuša attest to the presence of vibrant colors in the 2nd century Roman architecture at the site. The use of the various pigments suggested here may help to characterize the nature of the structure, or at least the resources utilized in its construction.

Abstract: Preservation of archaeological material must always be sensitive to the composition of the material itself. In this study, Portable X-Ray Fluorescence (Bruker Tracer IV SD) was used to provide non-destructive initial characterization of pigments on painted plaster fragments recovered from a 2nd century Roman building at Boğazköy-Hattuša. Including base plaster, ten different pigment profiles were identified, including lead-based and iron-based yellows, oranges, pinks, reds and browns, a copper-based blue-green, and organically based greens and browns.

¹⁴ Many of the pigments are lead-based, therefore licking to discover pigment presents many disadvantages.

VORLÄUFIGE QUALITATIVE ELEMENTARCHARAKTERISIERUNG VON FARBPIGMENTEN AUF
BEMALTEM PUTZ AUS EINEM RÖMISCHEN GEBÄUDE IN BOĞAZKÖY-HATTUŞA DURCH pXRF

Zusammenfassung: Die Erhaltung von archäologischem Material muss immer die Zusammensetzung des Materials selbst berücksichtigen. In dieser Studie wurde die portable Röntgenfluoreszenzanalyse (Bruker Tracer IV SD) verwendet, um eine zerstörungsfreie erste Charakterisierung von Pigmenten auf gemalten Putzfragmenten zu ermöglichen, die aus einem römischen Gebäude aus dem 2. Jahrhundert in Boğazköy-Hattuşa geborgen wurden. Den Basisputz eingeschlossen wurden zehn verschiedene Pigmentprofile identifiziert, darunter blei- und eisenbasierte Gelbtöne, Orange-, Rosa-, Rot- und Brauntöne, ein kupferbasiertes Blaugrün und organisch basierte Grün- und Brauntöne.

BOĞAZKÖY-HATTUŞA'DAN pXRF'YE KADAR OLAN ROMA YAPISINDAN BOYALI
ALÇI PİGMENTLERİNİN KALİTATİF İLKELE KARAKTERİZASYONU

Özet: Arkeolojik bir malzeme korunurken daima o malzemenin kendi yapısına duyarlı olmak gerekir. Bu çalışmada Boğazköy-Hattuşa'daki 2. yüzyıldan kalma bir Roma yapısından ele geçen boyalı sıva parçalarındaki pigmentlerin tahribatsız ön karakteristiğini temin etmek için Taşınabilir X-Ray floresanı (Bruker Tracer IV SD) kullanılmıştır. Alt sıva dâhil olmak üzere, kurşun temelli ve demir temelli sarı, turuncu, pembe, kırmızı ve kahverengi renkleri; bakır temelli mavi-yeşil ve organik temelli yeşil ve kahverengi renklerini içeren 10 farklı pigment profili belirlenmiştir.

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