The Matter of Chinese Painting, Case studies of 8th century murals

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Chapter 5

The Sample Analysis

Analysis of the 16 Samples from 4 Tang Tombs and 4 Samples from the Suilu'an

The ICN building in Amsterdam is a conglomeration of different-sized rooms, containing a variety of research instruments and specialists working these machines. Instruments, scientists and researchers cooperate in this building to conserve and protect the Dutch Art Collection. The ICN (Instituut Collectie Nederland) also engages in research beyond the confines of the Dutch collection, to broaden scientific knowledge about art objects from all areas of the world, and to provide conservationists with information. This provided me with the opportunity to perform the empirical scientific part of my research in the ICN laboratory. Karin Groen and Arie Wallert taught me the basics in one of their courses in Microscopy and Micro-chemical Analysis. From them, I learned that the methods involved in analysing and determining the different components of samples is a slow, step-by-step process of questions that sometimes lead to answers, and sometimes to more questions. For various reasons this research is unfinished and in fact, it may never be completely finished. Time limitations are a factor, but the main reason that this process continues to be ongoing is that the technical methods of research are always being developed, as scientists continue to seek improved research methods and instruments..

For this study, the samples were subjected to those tests best suited to the specific substance involved; not every method was therefore used on every sample.
The methods that were applied in this study are divided in the following 5 categories:

1. Microscopy
2. Chemical analysis
3. HPLC [a number of samples of 'modern' paint now available in shops in China are also analyzed with HPLC for comparison.]
4. X-Ray diffraction
5. SEM-EDX

The steps of analysis of the samples

The general steps taken in treatment of the samples are described for 20 samples, named:

YD1, YD2, YD3, YD4, YD5
YT1, YT2, YT3, YT4, YT5
ZH1, ZH2, ZH3,
ZQX1, WM1, WM2
SLA1, SLA2, SLA3, SLA4

As described in Chapter 4, at the time the samples were taken they were marked with their name; for example, the first sample taken in the tomb of the Crown Prince Yide is called YD1, the next sample is YD2 and so on.
At a later stage, when a small section is taken from the original sample, this part of a sample gains an addition to its name; YD1a, YD1b and so on; in this way the preparation can always be traced back to the original sample.
However, there are some exceptions to this rule, when the smaller parts of samples are given a different name. For example, the vials prepared for HPLC have names that are related to their location in the series of tests they undergo. All this makes evident just how vital careful bookkeeping is for this kind of research.

I will here firstly describe the general steps of the research process, in order to give an overall view of the factors involved. I will then use two specific samples, ZQX1a and ZQX1b, as examples with which to provide a detailed account of the handling of a sample.

The general steps in the process, marked I - VII

I. To begin with, I used the stereomicroscope to closely observe each sample. The separate layers in the sample show up clearly under this kind of microscope, as it allows a view with a great relative depth, which means that you have a three dimensional view of the sample in focus. The working distance between the lens of the microscope and the placing of the sample makes it possible to divide the samples into very tiny separate parts. From each of the layers in the sample a small part was scraped off and put on a hollow microscope slide or in a

vial. All were then carefully sealed to prevent contamination from the surroundings or handling.
Secondly, each of these smaller parts of the samples was marked and registered for further analysis. From a starting point of 20 samples, after separation the work space was now filled with around 100 laboratory slides and 34 small vials.

II. For the preparation of cross sections, a small part of each sample was cut off and embedded in polyester. I used Poly-pol PS 230 with catalyst 20 gram on 16 drops.
Once dry, each small polyester block, about 1cm x 1cm x 0.5 cm, was carefully taken down to the embedded sample by a slow process of grinding with increasingly fine sandpaper. After finely polishing the sample, it was now ready for examination under the microscope. The various objectives of the polarization microscope enable information about the different layers to be revealed. UV lighting makes it possible to detect organic components.
Samples of which cross sections were made are:

YD1,YD2A,YD2B, YD3, YD4A,YD4B,YD5
YT1,YT2,YT3,YT4B,YT4A,YT5
ZH1, ZH2, ZH3
ZQX1
WM1,WM2

[For a photograph of a cross section see chapter 4, p 133; photograph 4-02]

III. Preparations on microscope slides are embedded in Permount for further microscopic examination. These preparations are compared with my own reference collection of pigments that have been tested and positively identified.
Samples embedded in Permount:

ZQX1, ZQX2
ZH3B
YT3A, YT4A, YT5B
YD1A, YD2A, YD3A, YD3C, YD4B
WM1/6A
SLA1B, SLA2B

IV. Vials are filled with minute scrapings of each separate layer in the stratosphere of the samples. 14 vials were prepared by Maarten van Bommel for analysis of the binding media.
Samples scraped into vials:

ZQX1a, ZQX1b

ZH1b, ZH2a

YT1b, YT2b, YT5a

YD2a, YD3a, YD3b, YD4a, YD5a

SLA3, SLA4

A second batch of 4 vials was tested later:

ZQX1, ZH3, ZH2b, YD1

V. Five cross sections of the samples were taken to the Shell research laboratory, and with the help of Kees Mensch examined with SEM.
Samples examined by Kees Mensch en Lucien van Valen with SEM:

YD1, YD3

YT3, YT5

ZH2

One cross section of a sample was examined by Muriel Geldof and Kees Mensch with SEM at the Shell research laboratory.
Sample examined by Kees Mensch and Muriel Geldof with SEM:

ZXQ1

Fourteen cross sections of the samples were examined with SEM with the help of Ineke Joosten at the SEM facility of the ICN.
Samples examined by Ineke Joosten and Lucien van Valen with SEM:

YD2A, YD2B, YD4A, YD4B, YD5

YT4B, YT4A, YT2

ZH3, ZH1

ZQX1

WM1, WM2, WM-CLOTH

VI. X-Ray diffraction was performed on several samples by Peter Hallebeek at the ICN laboratory.

Samples subjected to X-Ray diffraction:

YD2B, YD4B
ZH2A
YT5A
WM1
ZQX1A

VII. Micro chemical analysis was performed on many of the separate layers of the samples. This is by far the most labor-intensive part of the process. In most cases the amount of material was extremely small, limiting the choice of wet analysis that I could perform. As described before, careful observation under the microscope gives a first indication of the mineral or minerals in the sample. This provided me with the questions that might be answered with wet chemical analysis.

In most cases I started with the behaviour of the sample towards acids: hydrochloric acid (3M HCl) and nitric acid (25 % HNO_3) and towards a caustic solution of 4M NaOH.

The ground layers

The test with HCl and with HNO_3 was used to identify the ground layers and to prove the presence of calcium carbonate $CaCO_3$ (chalk) or calcium sulphate $CaSO_4 \bullet 2H_2O$ (gypsum). For further identification of these calcium carbonate whites see Gettens et all, in 'Artists' Pigments', p 203 etc.

> Calcium Carbonate is, as such, the one of the easiest materials to identify by chemical and microscopical methods. It is more difficult to identify the specific varieties as recognition is largely dependent on study of the particle characteristics under the microscope.

In chalk the presence of coccoliths is characteristic. [see also chapter 4; photograph 4-05] The typical feature of small round particles with a cross are visible under the microscope and even better seen under the magnification of the Scanning Electron Microscope. Analysis with X-ray diffraction is also a positive means to identify the various calcium whites.

The pigment layer

For the identification of the elements in the pigment layer the separeted preparations made from the samples were subjected to a series of tests. Spot tests can be used on the samples to determine the metal contents of the minerals. For these tests the metal must be dissolved: first the sample is dissolved in an acid and slowly dried above a stove, and after drying the residue is dissolved in water or in a dilute acid solution. The sample is now ready for testing with the proper reagents to show a specific reaction.
I used several of the various test methods given by Joyce Plesters in *Studies in Conservation*, 1956. This publication includes a list of the solubility, effect of heat and specific tests for most of the minerals I found during this research.

Table 1

All samples were examined and handled under the microscope at the various stages of the research. Table 1 shows which preparations were subjected to testing with HPLC, SEM-EDX, XRD and Micro Chemical tests.

SAMPLE	LAYER	MATTER	HPLC	SEM-EDX	XRD	Micro-Chemical
YD1	1	maicaoni		X		X
	2	mianhua		X		
	3	baitu		X		X
	4	red	2X	X		X
YD2	1	maicaoni	X	X		
	2	mianhua		X		
	3	baitu	X	X	X	X
	4	green 10µm-50µm		X	X	X
YD3	1	maicaoni	X	X		X
	2	mianhua		X		X
	3	baitu	X	X		X
	4	red		X		X
YD4	1	maicaoni	X	X		X

SAMPLE	LAYER	MATTER	HPLC	SEM-EDX	XRD	Micro-Chemical
	2	mianhua		X		X
	3	baitu	X	X		X
YD5	1	maicaoni	X	X		X
	2	red		X		X
YT1	1	maicaoni	X	X		X
	2	mianhua		X		
	3	baitu		X		X
	4	red		X		X
YT2	1	maicaoni	X	X		X
	2	mianhua		X		X
YT3	1	maicaoni		X		X
	2	mianhua		X		
	3	baitu		X		
	4	Red 15μm-50μm		X		X
YT4	1	maicaoni		X		
	2	mianhua		X		
	3	baitu		X		X
	4	grey⇒ white + black		X		
YT5	1	maicaoni	X	X		
	2	mianhua		X		X
	3	baitu		X	X	
	4	red		X		X
ZH1	1	maicaoni	X	X		
	2	baitu		X		X
	3	red		X		
ZH2	1	maicaoni	X	X		
	2	baitu		X	X	X
	3	Red 20μm-40μm	2X	X		X
	4	transparent 10μm		X		
ZH3	1	maicaoni		X		

SAMPLE	LAYER	MATTER	HPLC	SEM-EDX	XRD	Micro-Chemical
	2	mianhua		X		
	3	baitu		X		X
	4	red	2X	X		X
ZQX	1	baitu	2X	X	X	X
	2	red 4μm-20μm-30μm	X	X	X	X
WM1/6	1	baitu		X	X	X

Sample ZQX1

I will now attempt to give the reader a better understanding of the different aspects involved in the process by following the sample ZQX1 during the whole period of research and the steps taken in this research process.

This sample comes from a mural from a Wei tomb that was excavated in an emergency. This sort of excavation always means that it has been removed very quickly, within a limited time and often under very tricky circumstances.

Zhang Qunxi, the chemist of the research laboratory of the Shaanxi History Museum, was working on this and other samples of the same tomb at the time I was working on my research in the Museum. For comparison with his own data he asked me to analyse this sample. The sample came to me with the following questions attached:

What is the nature of the binder?

Are there any organic components?

What is the nature of the paint layer ?

Is this haematite or minium?

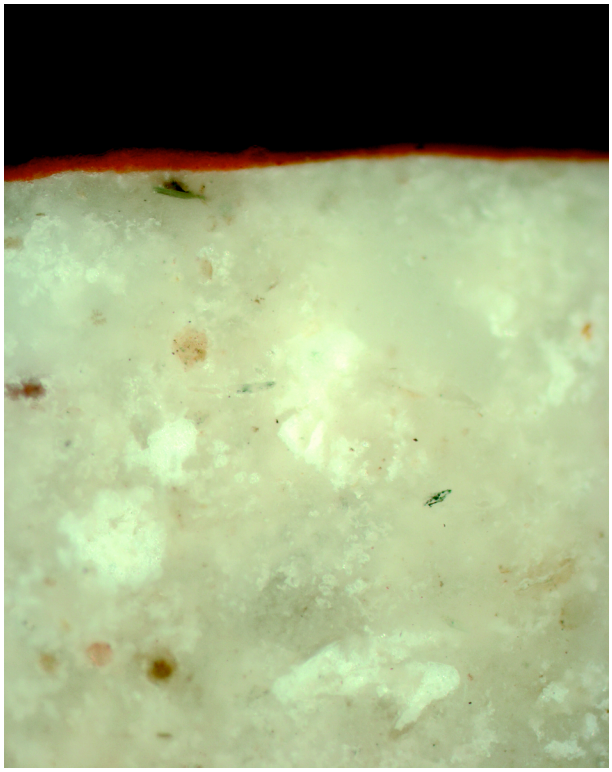
In addition to these, I myself posed the following question:

What is the nature of the ground layer ?

Observation under the Stereo microscope:

In the laboratory of the ICN in Amsterdam, I first put the sample under the stereomicroscope and saw a layered stratosphere:

- The first is a paint layer of an irregular, thin red brown, with craquelure; possiblly iron oxide.
- The second layer is white with small brown particles.



Photograph 5-01
Cross section of sample ZQX1; Magnification 200x.

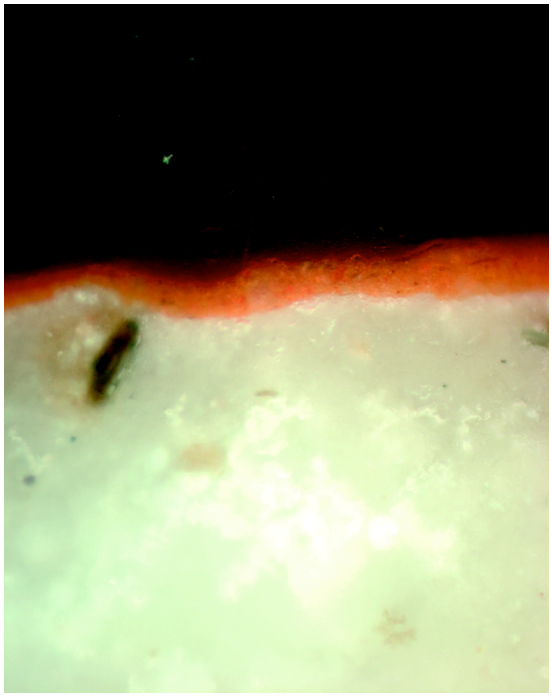
Preparation of vials:

Now vials were filled with very tiny parts of the two layers

- ZQX1a, ground layer, possibly loess and glue
- ZQX1b, red brown paint layer, possibly mineral and glue
- ZQX1c, fibre, possibly wood

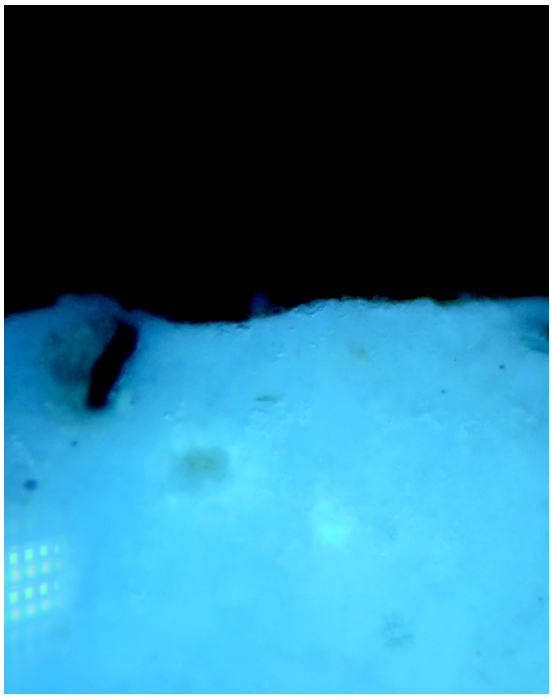
Preparation of a cross section:

A cross section of the sample was prepared in Poly-pol. This exposes the layer structure from the side, and allows a good view on this structure.



Photograph 5-02
Cross section of sample ZQX1; Magnification 500x.

Observation of the cross section under the stereo microscope:
Under the stereo microscope, the cross section showed that the paint layer was a bright red, with a darker brownish red at the surface. This may be a result of environmental influences. The thinner bright red layer was only 30 µm thick. In the white ground layer I could see some very fine fibres.



Photograph 5-03
UV Photograph of cross section of sample ZQX1
microscopic magnification 500x.

Second preparation of a Cross section:

A second cross section of the sample was prepared in Poly-pol.

Observation of the second cross section under the polarized light microscope:

The paint layer varies in thickness from 4μm to 20μm, and the small red particles measure 5μm. On the surface of the paint layer is a thin transparent layer. The white ground layer contains fine fibres.

HPLC testing for organic binders:

Two small parts were taken from the sample ZQX1 and named ZQX1a and ZQX1b. ZQX1a is the ground layer, ZQX1b is the paint layer. The samples were taken to Maarten van Bommel at the ICN, and analysed with HPLC as part of a larger batch of 14 samples.

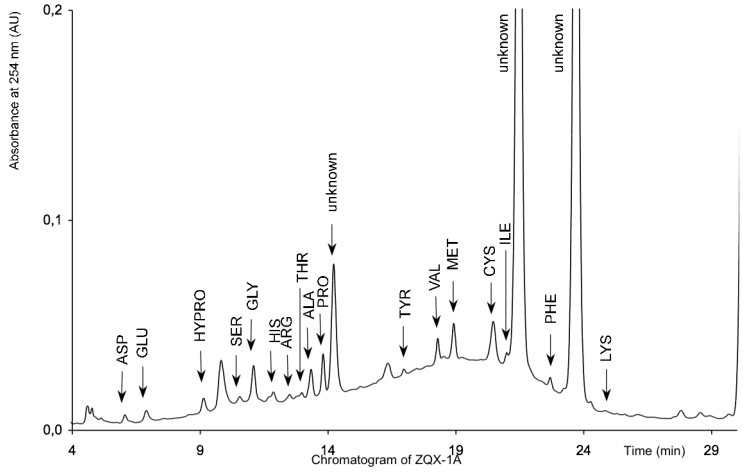
The use of the HPLC method as described by Maarten van Bommel:

> 14 samples are tested for amino acids to determine the protein contents. The analysis is complicated by the fact that a binder is found in a plaster layer, making it hard to determine the quantity of the binder. All samples are relatively large.
>
> Method description:
>
> To the samples (in vials) 250 μ 3 N hydrochloric acid is added. The samples completely dissolve in the hydrochloric acid. This produces carbon dioxide, which points to the presence of calcium carbonate. Subsequently the vials are sealed and the samples hydrolyzed at 105 ° C for 16 hours. This causes the protein to decompose into amino acids. After evaporation of the samples, phenyl isothiocyanate is added to react with the amino acids. This reagent is necessary to detect amino acids with UV absorption. After the reaction the samples are dried again and dissolved in the HPLC buffer and analysed. At an earlier stage the retention time of every individual amino acid is determined for identification. The proportion of the amino acid content indicates the kind of protein that is present in the sample.

The results of the samples ZQX1a and ZQX1b as described by Maarten van Bommel:

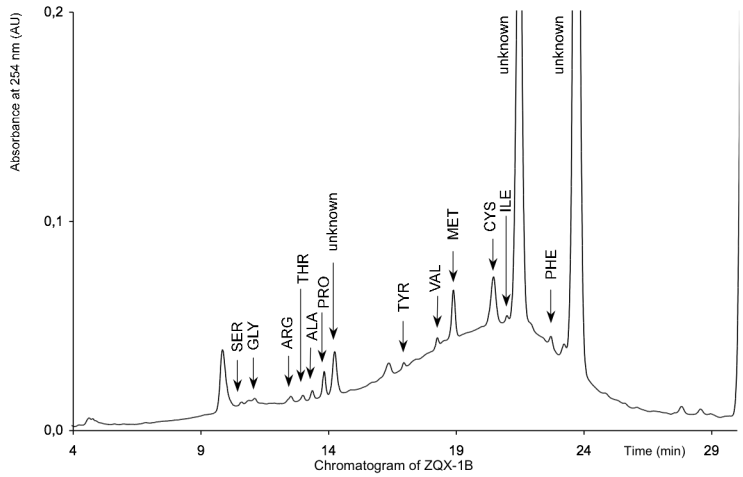
Amino acid	Area (%)	Amino acid	Area (%)
Aspartic acid	3.22	Proline	10.20
Glutamic acid	4.98	Tyrosine	1.48
Hydroxy-proline	5.23	Valine	5.80
Serine	1.95	Methionine	11.21
Glycine	13.76	Cysteine	19.24
Histidine	4.65	Iso-leucine	0.91
Arganine	1.81	Leucine	--
Threonine	2.06	Phenylalanine	2.70
Alanine	9.00	Lysine	0.93

'In this sample, almost all amino acids were detected. Identification is based on the presence of hydroxy-proline, which indicates the use of an animal glue. Unfortunately, it is not possible to distinguish between different animal glues. Three large peaks, marked as unknown, were found which can not be identified. These peaks were also found in sample ZQX-1B. The retention time of all amino acids are known, so these three peaks were definitely not indicative of amino acids. However, detection was performed at 254 nm, a wavelength at which much compounds shows absorption. Unmarked peaks were also detected in blank reactions (i.e. controls where the whole sample preparation procedure was followed without there being a sample), so these can be discounted as irrelevant.



Amino acid	Area (%)	Amino acid	Area (%)
Aspartic acid	--	Proline	12.70
Glutamic acid	--	Tyrosine	2.35
Hydroxy-proline	--	Valine	3.73
Serine	1.12	Methionine	25.02
Glycine	1.72	Cysteine	35.10
Histidine	--	Iso-leucine	1.72
Arganine	4.72	Leucine	--
Threonine	2.23	Phenylalanine	4.89
Alanine	4.70	Lysine	--

In sample ZQX-1b fewer amino acids were found than in sample ZQX-1a, probably due to the small sample size. Although a protein was found in this sample, identification of this protein was not possible. It is not known whether hydroxy-proline was absent or if it was not detected due to low concentration. The amount of methionine and cysteine is quite high; however, this could be an artefact.'



The results of my Chemical analysis:

The slide-mounted samples were now embedded in Permount, using the same method described in Chapter 4, for further microscopic examination and chemical tests.
The chemical analysis of ZQX1b [paint] was as follows:

First test:

- Hydrochloric acid (3N HCL)
  No effervescent reaction, light colouring on the outer rim
- Concentrated HCL
  Colour dissolves
- Dissolve in 3N HCL
- Add ammonium thiocynate
  Result: no red color!

Second test:

- 3N HCL
  Effervescent reaction points to $CaCO_3$,
  Small red particles remaining
- Ammonium thiocynate
  Result: Light red-coloured residue

Third test with a new red paint particle from the sample:

- 3N HLC
  Some effervescent reaction
  Red does not dissolve
- 3 x Concentrated HCL
  Result: forms a yellow rim

Two spot-tests on this yellow rim, one for Iron and one for Lead:

- Ammonium thiocynate
  Result: Positive for Iron:

Confirmation of Fe plus very fine particles, possible organic red present

- Potassium iodide 5 %
  Result: Negative for Lead: No Pb present

The chemical test for ZQX1a (ground) was as follows

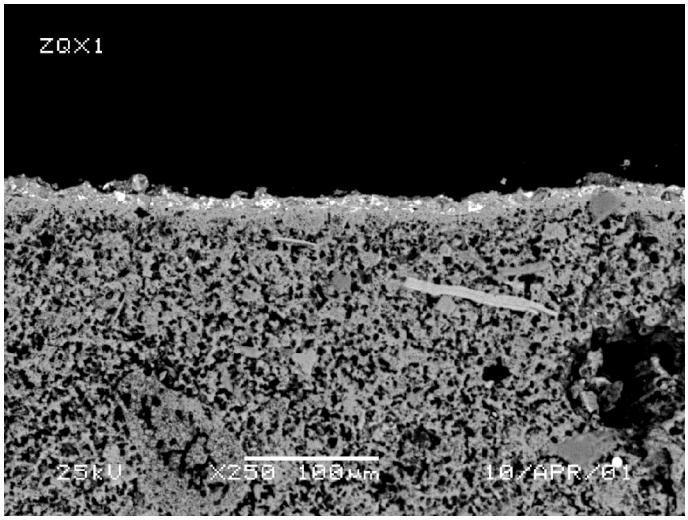
- 3N HCL
  effervescent reaction that
  confirms the presence of $CaCO_3$.

Next step:
The result of chemical tests of sample ZQX1a can be verified with X-Ray diffraction for the specific nature of the chalk.

X-Ray diffraction
Peter Hallebeek performed the X-Ray diffraction of a particle of the white ground layer of sample ZQX1.
The result was 80 % chalk-calcite and 20 % quartz in the ground layer. A very similar sample, WM1/6, comes from the same mural. It was taken from the protective cloth that was attached to the surface of the mural with peach gum upon removal during the emergency excavation of the tomb. WM1/6 gives the slightly different result of 100% chalk-calcite.

SEM

ZQX1a
The results showed the ground layer to be Ca with traces of Al, Mg and Si.
ZQX1b
The paint layer contains very fine iron particles measuring from 4 μm to 20 μm, spread in a 30 μm thick red-coloured layer. The layer also contains a large amount of Ca, and traces of Zn, Mg, Si and K.



Photograph 5-04
SEM photograph of the sample ZQX1.

The conclusion for ZQX1

After the interpretation of the results of all the tests performed on this sample the conclusion could be drawn that it has a thin layer of paint composed of a mixture of Haematite with a red organic colourant that is attached to a ground layer of calcite, most likely chalk.

Overview of the results of the samples

Table 2: the results of 14 samples tested by Maarten van Bommel, using the same method described above for the sample ZQX1.

no	Code	Description	Color sol. after hydrolysis	Result
1 a	ZQX1A	Ground layer loess	Colourless	Animal glue
2a	ZQX1B	Red-brown paint layer	Colourless	Protein, unidentified
4a	ZH1B	Grey layer	Light Yellow	Protein, unidentified
5a	ZH2A	White layer	Colourless	Animal glue
8a	YT1B	Loess layer	Yellow	Protein, unidentified
9a	YT2B	Loess layer	Yellow	Protein, unidentified
5b	YT5A	White ground layer	Colourless	Animal glue, plus possible fish glue
10b	YD2A	White ground layer	Colourless	Animal glue
2c	YD3A	White ground layer	Colourless	Animal glue

no	Code	Description	Color sol. after hydrolysis	Result
3c	YD3B	Grey ground layer	Yellow	No result
5c	YD4A	White render layer	Colourless	Animal glue
7c	YD5A	Yellow brown ground layer	Lost	------
3d	SLA3	Brown ground layer	Yellow	Animal glue
4d	SLA4	Loess from environment	Yellow	Animal glue

Table 3; The results of my chemical tests; note that chemical testing sometimes leaves a residue on the slide that does not dissolve in the acid that is applied.

Sample	Layer	Chemical result	Residue	Negative for
YD1	1	Fe^{3+}	small particles, red, grey, white	
YD1	3	$CaCO_3$		<$CaSO_4$
YD1	4	Fe^{3+}		<Pb
YD2	3	$CaCO_3$	white particles, transparent fluff	
YD2	4	Cu^{2+}		
YD3	1	$CaCO_3$, Fe^{3+}		
YD3	3	$CaCO_3$	particles; red, grey, white	
YD3	4	Fe^{3+}, S^2		
YD4	3	$CaCO_3$	brown, very fine particles spreading	
YD5	1	$CaCO_3$, Fe^{3+}	sand, large particles	
YD5	4	Fe^{3+}, S^2		
YT1	1	Fe^{3+}	sand, particles	
YT1	2	Fe^{3+}		
YT2	1	Fe^{3+}	sand, particles	
YT2	2	Fe^{3+}		
YT3	1	Fe^{3+}	sand, particles, quartz, blue particles	
YT3	2	Fe^{3+}		
YT3	3	$CaCO_3$	fluff of binder, particles: white/grey/red	

Sample	Layer	Chemical result	Residue	Negative for
YT3	4	Fe^{3+}, S^2	particles red 2 μm-5 μm, yellow 5 μm	
YT4	3	$CaCO_3$	possible paper?, black	
YT5	3	$CaCO_3$	hard yellow part, fluff of binder	
YT5	4	Fe^{3+}, S^2	brown particles	
ZH1	3	$CaCO_3$		
ZH2	3	$CaCO_3$	possible hemp?	
ZH2	4	Fe^{3+}		<Pb
ZH2	5	$CaCo_3$		
ZH3	3	$CaCO_3$		
ZH3	4	Fe^{3+}		<Pb
ZQX1	1	$CaCo_3$		
ZQX1	2	Fe^{3+}, Ca	red particles 5 μm	<Pb

SEM-EDX Spectra:

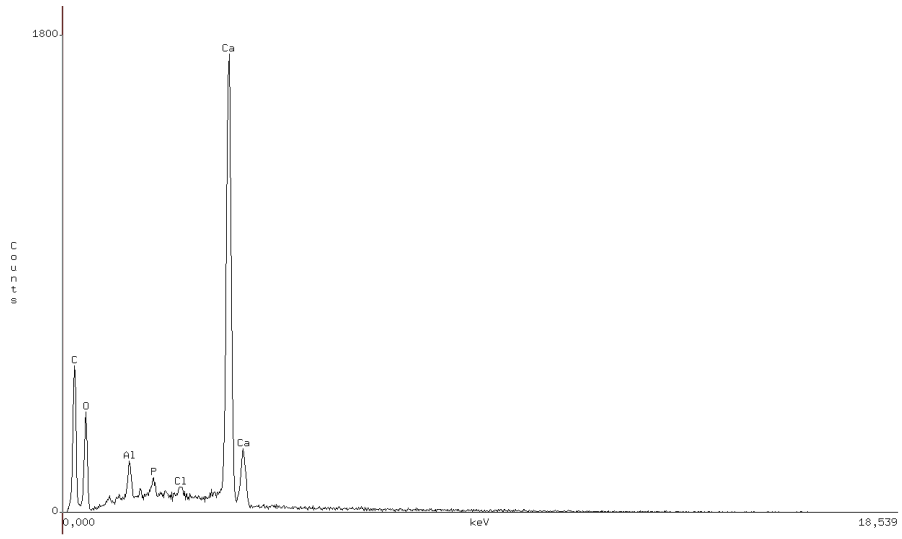
The SEM-EDX spectra shown are chosen to give examples of the various elements found in the research. Calcium, Aluminum, Magnesium and Silicates occur most commonly in the samples.

The assumption was that there would be alum, and to confirm this we were looking for potassium aluminum sulphate, which is a typical pointer for Alum earth. However, since there was a lack of sulphur in the samples this could not be established. The lack of sulphur might be due to the roasting of the alum earth in the production process.

Some samples do contain sulphur, but this is part of the vermilion paint layer. The combination of silicates with aluminum and potassium points in general to clays, and indeed some samples show the typical feather-like structure of kaolin in the ground layers. Another possibility is mica, such as muscovite that is a silicon: $KAl_2[(OH,P)_2|AlSi_3O_{10}]$; in sample YD4 all the chemical components are present.

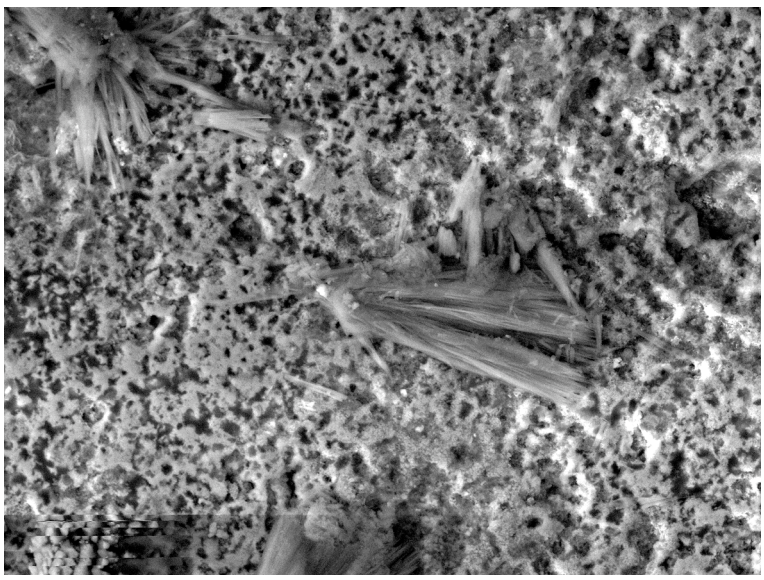
Figure 5-01, next page: The bulk layer of sample YD4A1 is a combination of Ca, C, O, Al, P and Cl. (calcium, carbon, oxygen, aluminum, phosphorus and chlorine**).**

Figure 5-01



YD4A1, bulklayer

Accelerating Voltage: 20 KeV
Take Off Angle: 34.3964°
Live Time: 100 seconds
Dead Time: 10.181

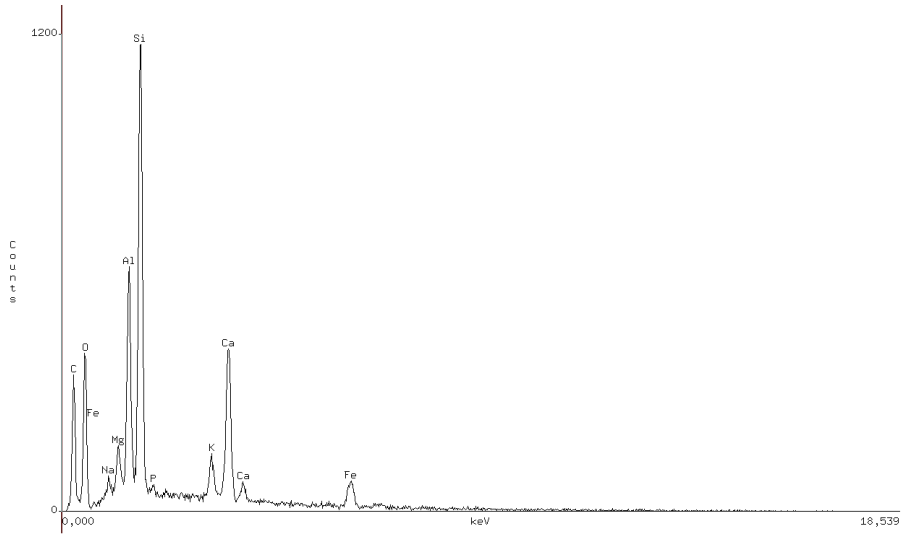


Photograph 5-05

SEM photograph of the ground layer of sample YD4;

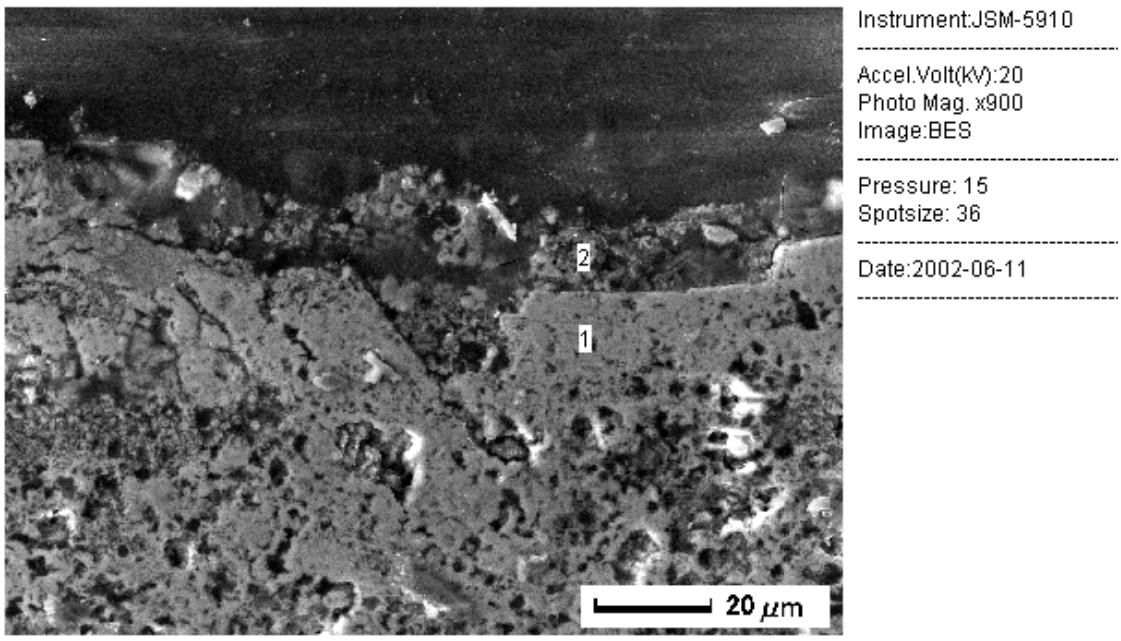
see also figure 5-01 and 5-02.

Figure 5-02: The paint layer of sample YD4A1 contains C, O, Na, Mg, P, Al, Si, K and Fe. (carbon, oxygen, sodium, magnesium, phosphor, aluminum, silicon, potassium, and iron)**.**



YD4A1, area1, paintlayer

Accelerating Voltage: 20 KeV Take Off Angle: 34.3964°
Live Time: 90 seconds Dead Time: 9.236



Photograph 5-06: SEM photograph of sample YT4: 1 is the ground layer; 2 is the paintlayer; see also figure 5-03, 5-04, 5-05 and 5-06.

The sample YT4

This is a very complicated sample, because it was taken from an area where white paint and black paint are touching or even overlapping each other in the paint layer. The SEM-EDX results show a combination of white paint that can be identified as
some form of calcite and black paint that proves to be graphite.

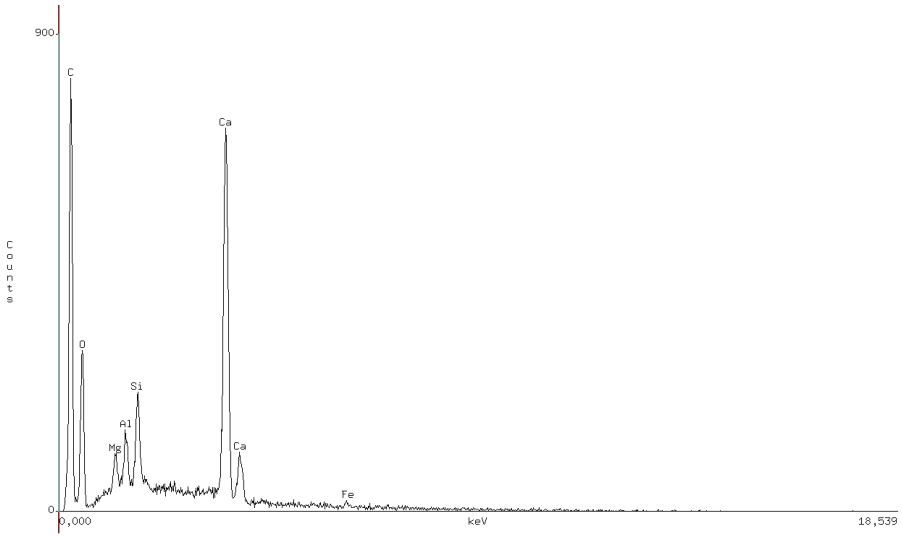
The analysis of an area measurement of the paint layer in cross section YT4A showed C, O, Mg, Al, Si, Ca and Fe. (a high carbon content with some oxygen, magnesium, aluminum, silicon, calcium and a trace of iron) *see figure 5-03 and 5-04*

The analysis of a spot measurement of the paint layer of cross section YT4A showed C,O,Ca,Al and Si. (carbon, oxygen and calcium with some traces of aluminum and silicon) *see figure 5-05*

The paint-spot measurement of sample YT4b showed Ca, C, Mg, O, S and Si (calcium, carbon, magnesium and oxygen with traces of sulphur and silicon) *see figure 5-06*

In the white ground layer were Ca, Si, C and O (calcium with a trace of silicon, and a small amount of carbon and oxygen).

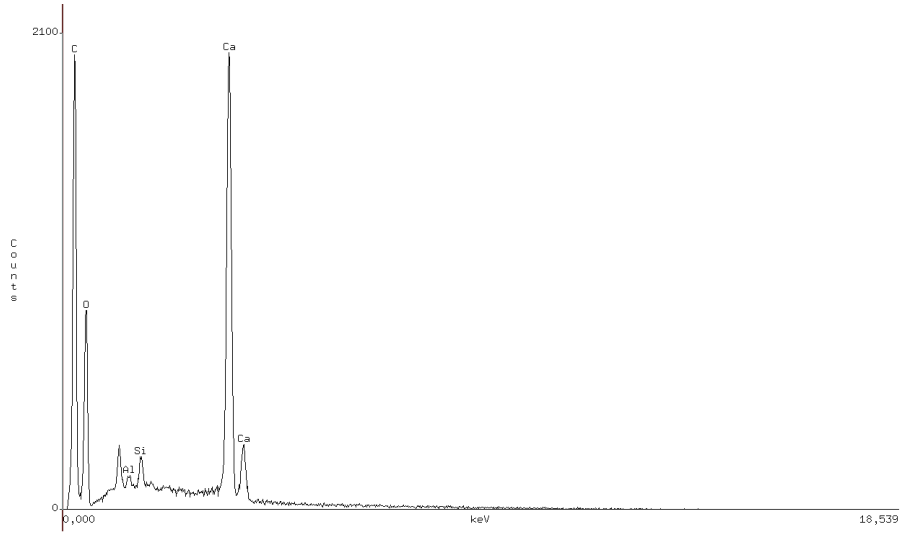
Figure 5-03



YT4A, area2, paint

Accelerating Voltage: 20 KeV Take Off Angle: 35.2985°
Live Time: 100 seconds Dead Time: 11

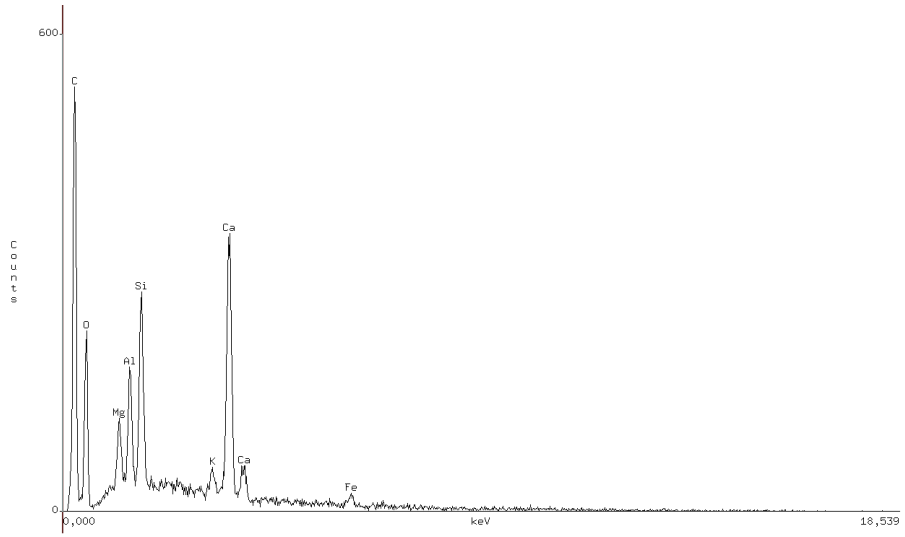
Figure 5-04



YT4b1, area2, paint layer

Accelerating Voltage: 20 KeV Take Off Angle: 35.6931°
Live Time: 80.51 seconds Dead Time: 8.3

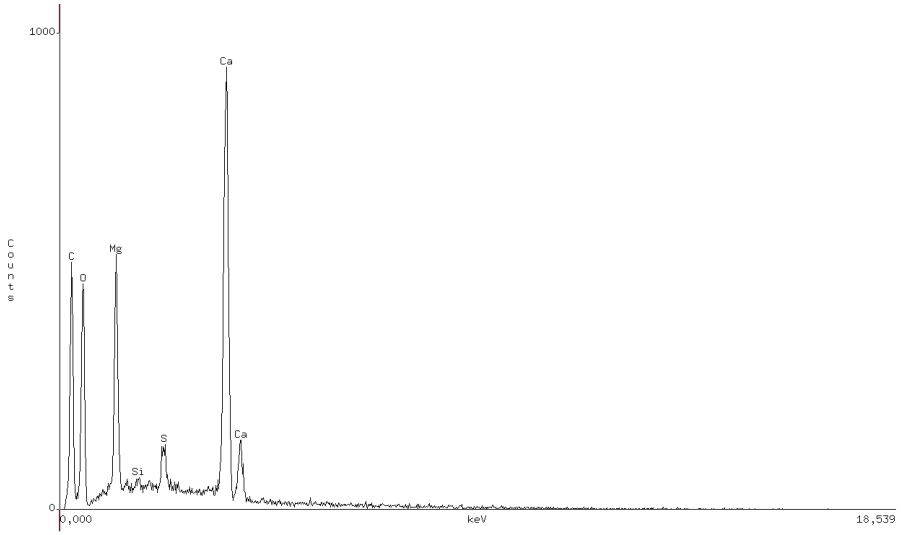
Figure 5-05



YT4A, spot1, paint

Accelerating Voltage: 20 KeV Take Off Angle: 35.2985°
Live Time: 75 seconds Dead Time: 12.34

Figure 5-06



YT4b1, spot1, paint

Accelerating Voltage: 20 KeV Take Off Angle: 35.6931°

Live Time: 80 seconds Dead Time: 8.814

In one other sample YT2 from this tomb I found a thin black top layer that is supposedly a contamination from the environment in the tomb. This layer of the sample YT2 turned out to be soot, probably from a fire or from torches used in the tomb at some point.

Photograph 5-07, left

Surface of the sample YT2 with soot particles. On the left a mumian fibre is visible

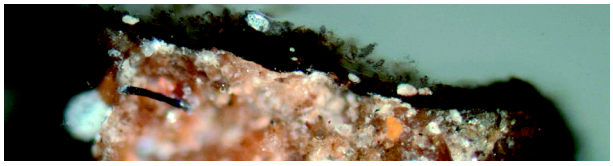
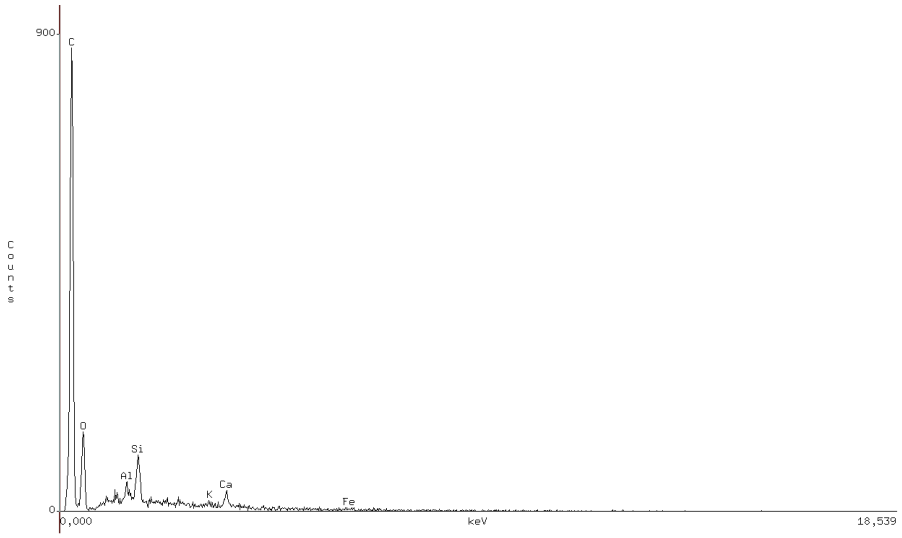


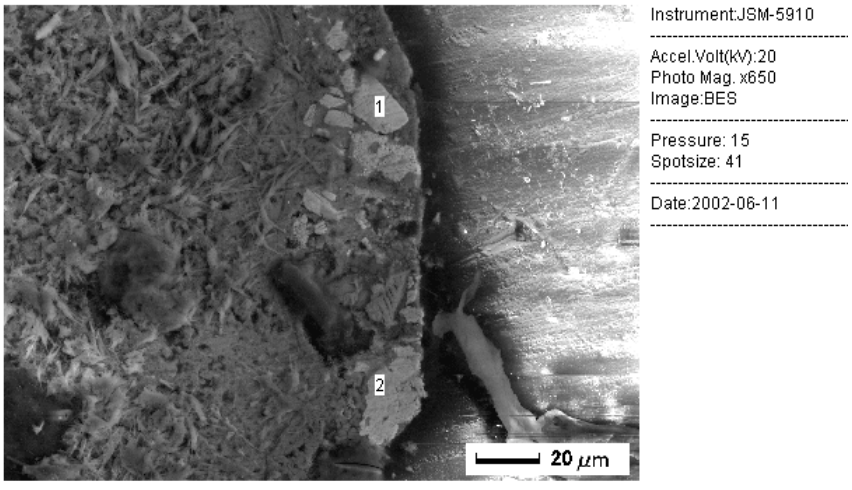
Figure 5-07



YT2, area2, soot

Accelerating Voltage: 20 KeV Take Off Angle: 34.0914°
Live Time: 40 seconds Dead Time: 5.847

The sample YD2a is a green paint: the copper content was clearly shown in the EDX-spectrum.

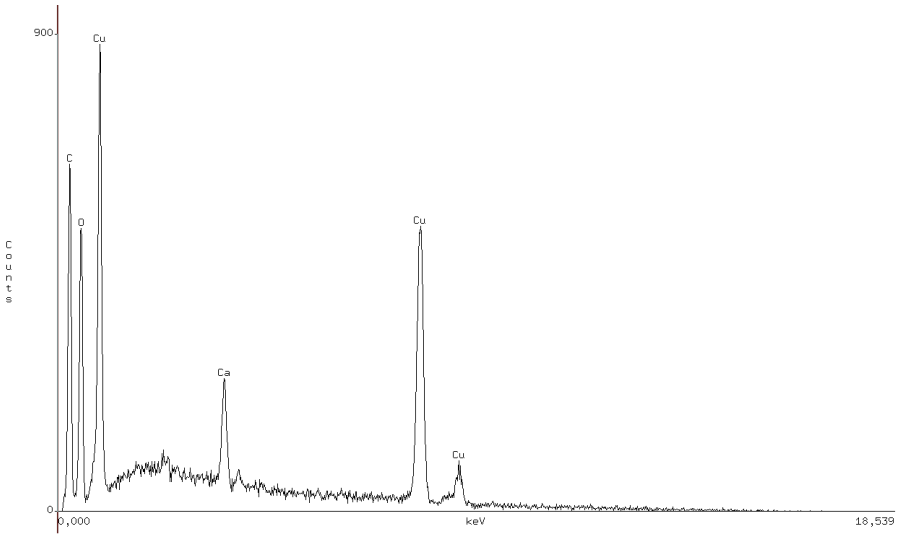


Photograph 5-08

SEM photograph of sample YD2: the location of two spot measures are indicated 1 and 2.

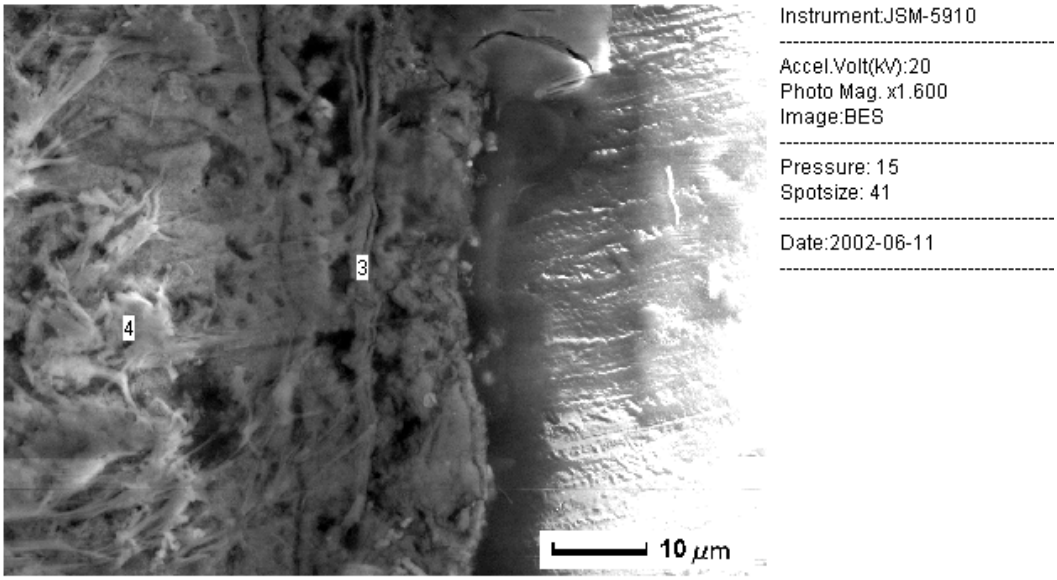
See figure 5-08 for spot measure 1.

Figure 5-07



YD2b, spot1, paint

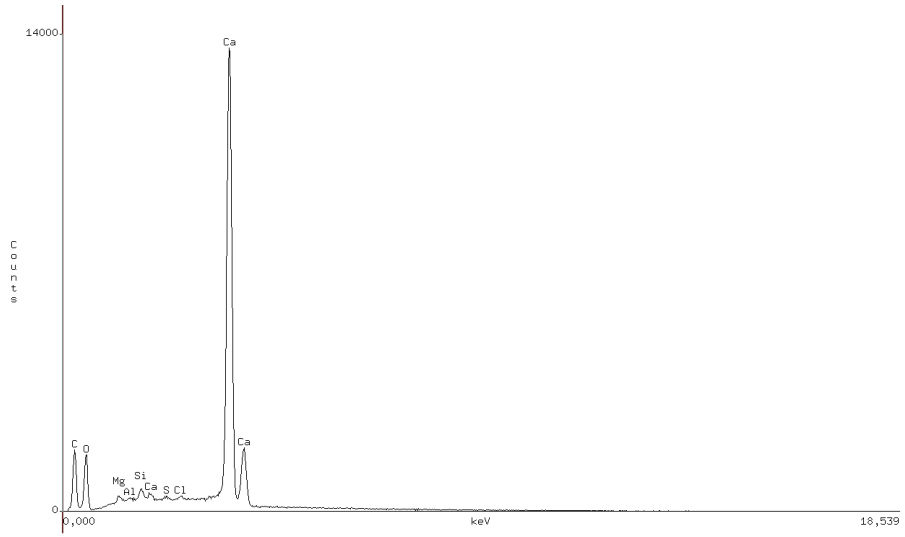
Accelerating Voltage: 20 KeV Take Off Angle: 33.9892°
Live Time: 44 seconds Dead Time: 7.894



Photograph 5-09, SEM photograph of sample YD2: the location of two bulk measures is indicated with 3 and 4. See figure 5-09 for bulk measure 4.

The bulk of the white ground layer in YD2a showed Ca, C, O, Mg, Al, Si, S and Cl. (calcium, carbon, oxygen, magnesium, aluminum, silicon, sulphur and chlorine)

Figure 5-09



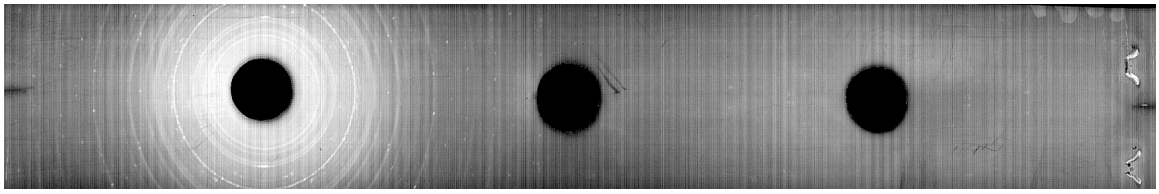
YD2a, bulk

Accelerating Voltage:	20 KeV	Take Off Angle:	35.1992°
Live Time:	100 seconds	Dead Time:	43.743

Table 4, SEM-EDX and XRD results.

SAMPLE	Layer	MATTER	SEM-EDX	XRD
YD1	4	Red ⇒transparent top	C,O,Fe,Na,Mg,Al,Si,P,S,Cl,K,Ti,Ca ⇒C,O,Fe,Na,Mg,Al,Si,Sr,S,Cl,K,Ca	
YD2	1	maicaoni	C,O,Mg,Al,Si,Ca,S,Cl	
	3	baitu	C,O,Mg,Al,Si,Ca,Cl	50%chalk-calcite 50%chalk-aragonite
	4	green 10μm-50μm	C,O,Cu,Al,Si,Ca,Zn	10%silicon 90%para-atacamite
YD3	3	baitu	C,O,Mg,Al,Si,Sr,Ca	
	4	Red spot⇒ ⇒transparent top	C,O,Al,Hg ⇒C,O,Mg,Al,Hg,Ca ⇒C,O,Mg,Al,Si,Ca	
YD4	1	maicaoni	C,O,Na,Al,Si,K,Fe	
	2	mianhua	C,O,Fe,Na,Mg,Si,P,K,Ca	
	3	baitu	C,O,Al,P,Cl,Ca	
YD5	1	maocaoni	C,O,Na,Al,Si,K,Ca,Fe	
YT2	2	mianhua	C,O,Al,Si,K,Ca,Fe	
YT3	2	mianhua ⇒spot grey	C,O,Mg,Al,Si,Sr,S,Cl,K,Ca,Fe ⇒C,O,Mg,Al,Si,S,Cl,Ca,Fe	
	4	Red 15μm-50μm spot1⇒ spot2⇒	C,O,Fe,Mg,Al,Si,Sr,S,Cl,K,Ca ⇒C,O,Sr,Ca ⇒C,O,Fe,Na,Mg,Al,Si,Sr,S,Cl,K,Ca	
YT4	2	mianhua	C,O,Al,Si,K,Ca,Fe	
	3	baitu	C,O,Si,Ca	
	4	grey⇒ white + black⇒	⇒C,O,Mg,Al,Si,Ca,Fe ⇒C,O,Al,Si,Ca	
YT5	2	mianhua	C,O,Mg,Al,Si,Sr,S,K,Ca	100%chalk-calcite
	3	baitu	C,O,Na,Mg,Al,Si,Sr,S,Cl, Ca	
	4	red spot1⇒ spot2⇒	C,O,Na,Mg,Al,Si,Sr,S,K,Ca ⇒C,O,Na,Mg,Al,Si,Hg,S,K,Ca,Fe ⇒C,O,Na,Mg,Al,Si,Hg,K,Ca,Fe	
ZH2	2	baitu	C,O,Fe,Mg,Al,Si,S,Cl,Ca	100%chalk-calcite
	3	Red 20μm-40μm	C,O,Fe,Al,Mg,Si,Sr,K,Ca,Fe	
	4	transparent 10μm		
ZQX1	1	baitu	C,O,Mg,Al,Si,K,Ca,Fe	
	2	red 4μm-20μm-30μm	C,O,Fe,Zn,Mg,Al,Si,K,Ca,Ti,Fe	
WM1/6	1	baitu	C,O,Cl,Ca	100%chalk-calcite
WM1/6	2	red	C,O,Fe,Al,Si,K,Ca	

Photograph 5-10: XRD spectrum of the paint layer of sample YD2.



XRD by Peter Hallebeek:

The results of X-Ray diffraction for YD2 showed a spectrum for copper.

This sample's ground layer differed from all other ground layers in the samples in its aragonite component. The X-Ray diffraction test for a minute particle of this sample YD2 showed 50% chalk and 50% aragonite. *See Photograph 5-10 on page 156.*

Table 5, The Mineral and Organic content of the different layers:

Sample	Layer	Matter	Substance	Mineral	Organic
YD1	1	*maicaoni*	*huangtu*	Fe	straw
	2	*mianhua*			cotton fibre
	3	*baitu*	chalk	$CaCO_3$	
	4	red	iron,	Fe, unknown red ⇒ neg:Pb	organic, unknown flavonoid
YD2	1	*maicaoni*	huangtu		straw
	2	*mianhua*	huangtu		cotton fibre
	3	*baitu*	chalk, aragonite	$CaCO_3$: 50% chalk, 50% aragonite	animal glue
	4	green 10µm-50µm	para-atacamite	90% $Cu_2(OH)_3Cl$ 10% silicon	
YD3	1	*maicaoni*	grey	$CaCO_3$, Fe	no amino acids
	2	*mianhua*	*huangtu*		cotton fibre
	3	*baitu*	chalk	$CaCO_3$	animal glue
	4	red	iron, vermilion	Fe, S^2 [sulphur> vermilion]	
YD4	1	*maicaoni*	*huangtu*		straw

Sample	Layer	Matter	Substance	Mineral	Organic
	2	*mianhua*	*huangtu*		cotton fibre
	3	*baitu*	chalk	$CaCO_3$	animal glue
YD5	1	*maocaoni*	chalk, iron	$CaCO_3$, Fe	HPLC>lost, white fibre, straw
	2	red	iron, vermilion	Fe, S^2 (sulphur> vermilion)	
YT1	1	*maicaoni*	*huangtu*	Fe	unidentified protein
	2	*mianhua*	*huangtu*	Fe	cotton fibre, unidentified white fibre
	3	*baitu*			
	4	red			
YT2	1	*maicaoni*	*huangtu*	Fe	unidentified protein, straw, long white fiber
	2	*mianhua*	*huangtu*	Fe	cotton fibre
YT3	1	*maicaoni*	*huangtu*	Fe	
	2	*mianhua*	*huangtu*	Fe	
	3	*baitu*	chalk	$CaCO_3$	
	4	Red 15μm-50μm	vermilion	Fe, S^2 [sulphur>vermilion]	
YT4	1	*maicaoni*	*huangtu*		
	2	*mianhua*	*huangtu*		cotton fibre
	3	*baitu*	chalk	$CaCO_3$	
	4	grey⇒ white + black	black white	C, $CaCO_3$	
YT5	1	*maicaoni*	*huangtu*		
	2	*mianhua*	*huangtu*		cotton fibre
	3	*baitu*	chalk	$CaCO_3$, 100% chalk	animal glue, possible fish glue
	4	red	vermilion	Fe, S^2 [sulfur> vermilion]	
ZH1	1	*maicaoni*	*huangtu*		unidentified protein
	2	*baitu*	chalk	$CaCO_3$	
	3	red			

Sample	Layer	Matter	Substance	Mineral	Organic
ZH2	1	*maicaoni*	*huangtu*		
	2	*baitu*	chalk	$CaCO_3$, 100% chalk	animal, unidentified fibre: hemp?
	3	Red 20μm-40μm	iron	Fe	
	4	transparent 10μm		$CaCO_3$	
ZH3	1	*maicaoni*	*huangtu*		
	2	*mianhua*	*huangtu*	cotton fiber	
	3	*baitu*	chalk	$CaCO_3$	
	4	red	iron	Fe	
ZQX	1	*baitu*	chalk, quarts	SEM> Ca, XRD> 80%chalk, 10% quarts,	unidentified fibre: hemp?
	2	red 4μm-20μm-30μm	iron, chalk, silicon	Fe, Ca, Si	unidentified protein, organic dye

Modern reference materials

For reference, a number of tests were performed on some modern ‘traditional’ paint materials, in order to provide comparative material. In reality, the results up to this point have been mostly inconclusive and contribute only to show once more the complicated structure of Chinese paint. These modern paints are sold as being made of traditional materials, and are probably just that. At the department that is responsable for the production of paint at the Beijing Middle School of Fine Art I found a number of paints that had supposedly been prepared using traditional methods. The proprietor kindly handed me some pieces of mineral: azurite and malachite. These two small lumps of mineral are indeed a good reference for research. However, the paint in glass bottles labelled 'rouge', 'sap green' etc all proved to be of an indistinguishable substance. In testing them, we found many unidentified components, making the determination of the true nature of these so-called ‘traditional’ paints very

difficult. This meant that unfortunately we have had, for now, to disqualify them as reference material. For this reason, I came to the conclusion that collecting a reference collection of the raw substances used in the paint is of the utmost importance. The collection of these specimens is a process that is still ongoing, and includes finding and identifying mineral, vegetable or other components. This is in addition to the search for samples of traditional paint and identifying their often complex composition. The building of a reference collection will be the focus of future research. Since this part of the research has not yet been completed its scope is therefore very limited. A short list of results is included below, which clearly illustrates the complexity of this kind of research.

Modern Paint tested using HPLC by Maarten van Bommel

Table 6, Results of the reference samples:

sample	name	translation	Result	Conclusion
M1	*Yanzhi*	Rouge-1	Ponceau-like (r) Metanil-yellow-like (g) Chrysoin-like (r) 2× kermes acid like (r) 2 unknown yellows 1 unknown red	Rather impure sample. Probably something synthetic or a composite of various synthetic colourants.
M2	*Yue huang*	Moon yellow-2	6 yellow components that all are found in Camboge. Trace of an unknown red component.	Camboge
M3	*Yanzhi-2*	Rouge-3	Caesalpinia sappan peek: Brasileïne Alizarin Munjistin-like Purpurin Purpurin-like	Composite of Brazil wood and madder, likely to be Indian madder (*Rubia cordifolia L.*)

sample	name	translation	Result	Conclusion
M4	*Zhihuang*	Sap green-4	Quercetin-like (92%) Kampferol (2%) Quercetin-like (6%)	Unknown flavonoid colourant
M5	*Lücao huang*	Green yellow-5	No result	--
M5-Hac	*Lücao huang*	Green yellow -5	Rutin Rhamnetin	Rutin is typical for South-East Asia and is found in many plants, i.e. Chinese berries (*Sophora japonica, floss*), Buckwheat (*fagopyrum esculentum, herba*) and many others.
M6	*Zibiao*	Shellac-6	No result	NOT shellac!!
M6-Hac	*Zibiao*	Shellac-6	Rutin Rhamnetin	See M5-Hac
M7	*Zhihuang*	Sap yellow-7	3 unknown flavonoides 3 curcuma-like	Unclear, test again with Hac
M8	*Caohuang*/ yellow	Grass yellow-8	Kampferol 2× quercetin-like	?
M8-Hac	*Caohuang*/ yellow	Grass yellow-8	4 morin-like quercetin-like fisetin-like	Could be something like the Jack-fruit plant (*Artocarpus heterophyllus LAM.*) or white mulberry (*Morus alba L.*)
M9	*Caohuang*/ grey	Gras yellow-9	No result	--
M9-Hac	*Caohuang*/ grey	Gras yellow-9	No result	--