国际标准连续出版物号　ISSN 1000-7954
国内统一连续出版物号　CN 61-1009/K

全国中文核心期刊

文博

2009
总153期　第6期

目　录

双月刊

2009年第6期（总第153期）

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国际标准连续出版物号　ISSN 1000-7954
国内统一连续出版物号　CN 61-1009/K
国内总发行　陕西省邮政报刊发行局
邮发代号　52-74
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The Matter of Chinese Painting

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Abstract: This research includes the analysis of painted samples from the Tang Murals of the Qianling Mausoleum, the non-destructive analysis of Yuan and Ming Paintings in the collection of the Freer gallery and the analysis of painted samples from a Yuan Mural in the collection of the Rijksmuseum in Amsterdam. The samples were compared with the collection of samples about classic Chinese painted material and Chinese raw minerals, pigments and plants.

Key words: Matter; Chinese Painting; Pigments and plants

1 Introduction

Chinese painting materials have been researched with different methods. The paints used on statues in most cases are similar to the paints that are used on murals, on silk and on paper. This research includes the analysis of painted samples from the Tang Murals of the Qianling Mausoleum, non-destructive analysis of Yuan and Ming Paintings in the collection of the Freer gallery and analysis of painted samples from a Yuan Mural in the collection of the Rijksmuseum in Amsterdam. The samples were compared with the collection of samples about classic Chinese painted material and Chinese raw minerals, pigments and plants. The terminology used for the various materials is complicated and can be traced trough the long history of China. Several books, such as The Erya, Useful things for the People (齊民要術), Record of Famous Chinese paintings (歷代名畫記), Research of Traditional Chinese Painting materials (中國畫顏色的研究), and many other books, have been used in this research to define an accessible terminology of the paints and other materials. In view of international cooperation in conservation a consensus for the translation of these terms is of the utmost importance. All the information will be made available on the internet, and currently a first draft of two tables with chemical formula and names in Chinese and English can be found on my internet site: http://www.hinamatters. nl, see 'Terms 1', 'Terms 5', and 'Chinese colour names'.

2 The painting technique in Tang dynasty

Fixed markers of painting technique are the Qianling tomb paintings of the early Tang dynasty. They are of undisputed age and have several pieces left in situ that are relatively undisturbed. Taking of samples of the paint layer and the underlying structure of the ground layer was the first step. The information collected has been described in detail in my thesis: The Matter of Chinese Painting, Case studies of 8th century murals [1]. The book is available for downloading in PDF-format on the internet: http://hdl.handle.net/1887/3730.

2.1 Ground layer

To prepare the wall for painting, several ground layers have been applied. The first layer consists of mud to prepare the wall, and is about 1 to 2 cm thick. The main component is loess or yellow earth (*huangtu* 黄土) containing iron, sand and some quartz. In the case of the three Qianling tombs this first layer is a mixture of loess and wheat straw (*maicao* 麦草), see Fig.1. Today this mixture is still used for plastering walls. Present-day samples taken for reasons of comparison are exactly the same as the samples from the 8th century.

The results of HPLC analysis proved that in this first layer glue is added. In some samples, the loess layer contains animal glue, and other samples contain a protein to be identified. The presence of coccoliths identifies chalk in the layer. The glue is a combination of all available animal bone and skin parts, as we can

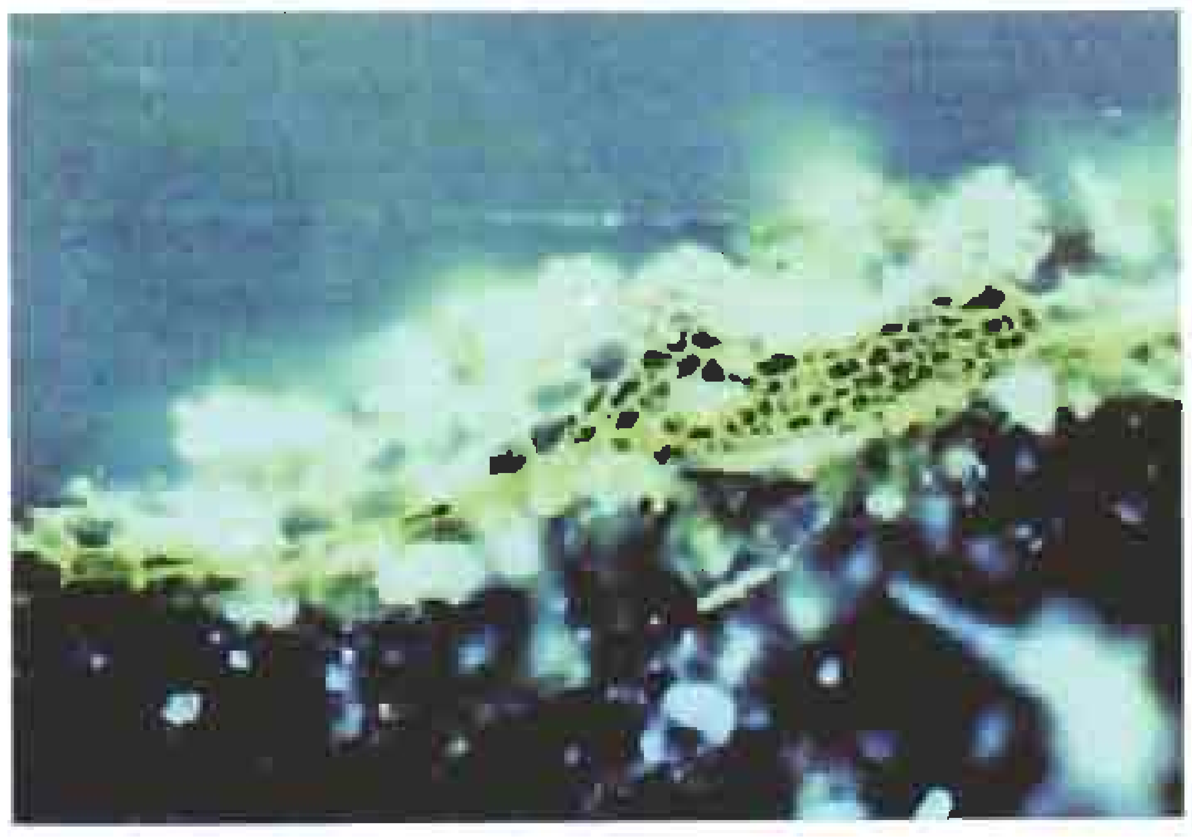


Fig.1 Microscope photograph of the straw fibre in the ground layers of the wall in the Yong Tai tomb under UV light, magnification 200x

Fig.2 Microscope photograph of a fibre: straw mud, tree cotton, magnification 200x

Fig.3 The feathery structure is clay and the round forms are chalk coccoliths in sample ZH3, magnification 500x

derive from the description of one of the glue-making methods in the farmer's handbook *Useful things for the People* (*Qimin yaoshu in Chinese*, 齊民要術)[2].

Two of the three tombs have a second preparation layer. The first layer with the wheat straw, wheat straw that is mixed with yellow-earth to form the so-called straw mud (麦草泥). Above that is a second yellow-earth layer that contained several kinds of fibre. In the Yong Tai tomb these fibres are present in all the samples, see Fig.2.

Furthermore, in the Yi De tomb all the samples that were taken from the top-layers contain the same fibres. This is the three cotton fibre (*mumian* 木棉). These layers are a mixture of loess, yellow earth and three cotton fibres, and together they form a 'cotton mix' layer. The same fibres are present in the white plaster-layer of the Yong Tai tomb.

The common cotton plant as we know it these days was only introduced in China during the Tang dynasty[3]. There is confusion about the nature of 'cotton' because in written sources it is hard to differentiate between the Chinese indigenous *mumian* cotton fibres and the later imported common cotton. The indigenous cotton can better be called 'tree cotton' to make a clear distinction between the two types.

The third layer is a whitewash one, it is made of a fine white ground to smooth the surface and prepare it for the final painting. Calcium carbonate is present in all samples, but there are slight variations in the composition. For example in the Yi De tomb X-ray diffraction shows 50% chalk + 50% aragonite and this is confirmed by chemical testing. This aragonite must originate from a maritime source, either an ancient cretaceous deposit or a contemporary shell component. For comparison, in the *Shuilu'an*-a temple in Lantian near Xi'an-some of the impasto lines show aragonite that is mixed with lead white. This aragonite is clam white[4]. I will come back to the clam white later.

There are particles of various other elements such as Silicon, Potassium, Calcium, Sulphur, Aluminium, Iron and traces of Magnesium and Titanium, which indicate a clay component or a mica component[5]. The results show also that a mixture of chalk and clay is used, see fig.3. One fact stands out in this layer: no matter what the different components are of these white ground layers, all the white-layer samples from the three tombs that were examined are mixed with animal glue. In the white layer of some samples finer hemp fibres are present, sometimes mixed paint is used, and some parts of the walls are painted on only one single preparation layer.

In the Yong Tai tomb, fish glue is found in a chalk layer (fig.4 and fig.5). Since the chalk layer is similar to the others, the type glue must be used for a special reason. Maybe it is related to the colour layer.

Fig.4 The ground layer of sample YT5 shown fish glue, magnification 500x

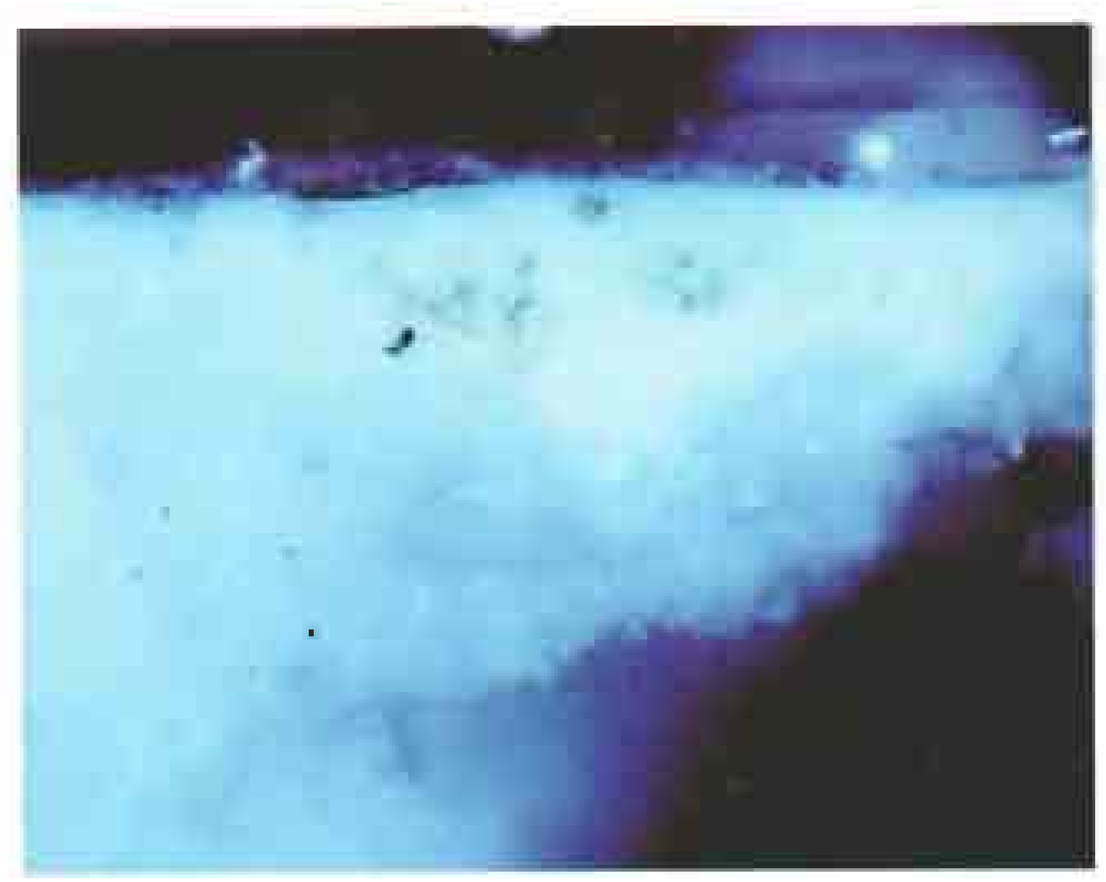


Fig.5 UV photograph of a cross section of sample YT5, magnification 200x

2.2 Pigments

(1) Iron oxide

Iron oxide is by far most frequently present, but sometimes the paint is a mixture, containing other organic components beside the glue, which is essential to attach the pigment to the white surface. On the curved ceiling in the corridor of the Yong Tai tomb the red paint layer is very thin [30 μm], see Fig.6. This is cinnabar mixed with iron oxide, clay and chalk and it also contains glue and traces of alum. The top of the paint layer shows an almost transparent, very thin surface layer of chalk. This transparent layer is only visible in the cross section under the microscope and it does not influence the strength of red colour. The layer is a mixture of chalk, clay and glue.

In the Yide tomb, a red paint layer that is a mixture of cinnabar with iron oxide and chalk was also found (Fig.7, 8 and 9). Lead is significantly absent in all red paint samples that were also subjected to chemical spot test for lead and all came out negative.

A red paint layer with traces of an organic dye was found in the Zhang Huai tomb (Fig.10 and 11). This red paint is soluble in water due to its organic dye component. The sample is a mixture organic red with chalk, iron oxide, and glue. The red organic dye could be safflower, dragon blood, or stick lack.

(2) Cinnabar, vermilion or mercuric sulphide

We now take a short detour to a written source. At this point we look at the book "The research of Chinese traditional painting materials" [6] written by Yu Fei'an in the fifties of the last century. Yu Fei'an was the first to attempt a scientific approach to define the matter of paint. He describes the way to separate the grains of cinnabar and malachite into different colours based on the size of the grain.

Cinnabar, vermilion or mercuric sulphide is one of the oldest known mineral reds (Fig.12). In China, it is found in its mineral form in Hunan, Guizhou, Sichuan and Yunnan. In Chinese painting, it is one of the earliest known mineral colours. It is a mercuric sulphide. The Chinese make a difference between natural cinnabar and the mercuric sulphide that is

Fig.6 Cross section of sample YT5, magnification 500x

Fig.7 The location from which sample YD3 was taken

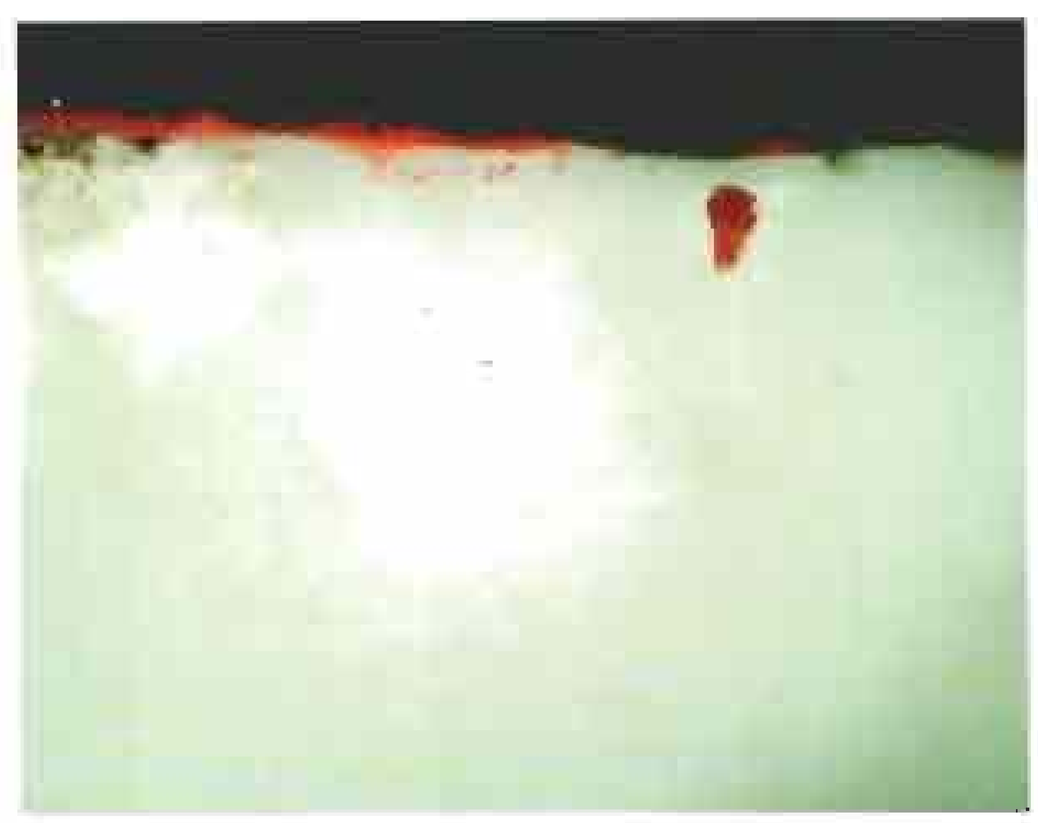


Fig. 8 Cross section of sample YD3, showing a remarkable, small spot of lead in the chalk layer. No other traces of lead in any form are present in the samples of the three Tang tombs

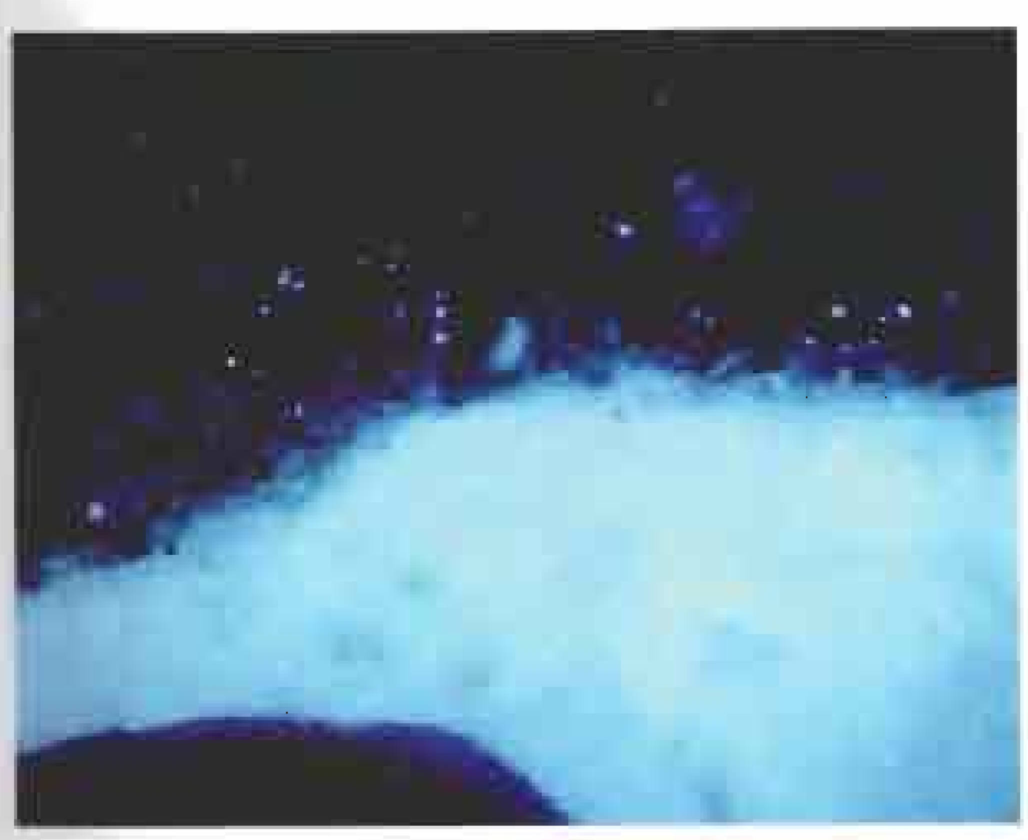


Fig.9 Under UV light the fibres are clearly visible in the layer of losses, yellow earth mixed with three cotton fibber, cotton fibre in this ground layer of the cross section of sample YD3, magnification 200x

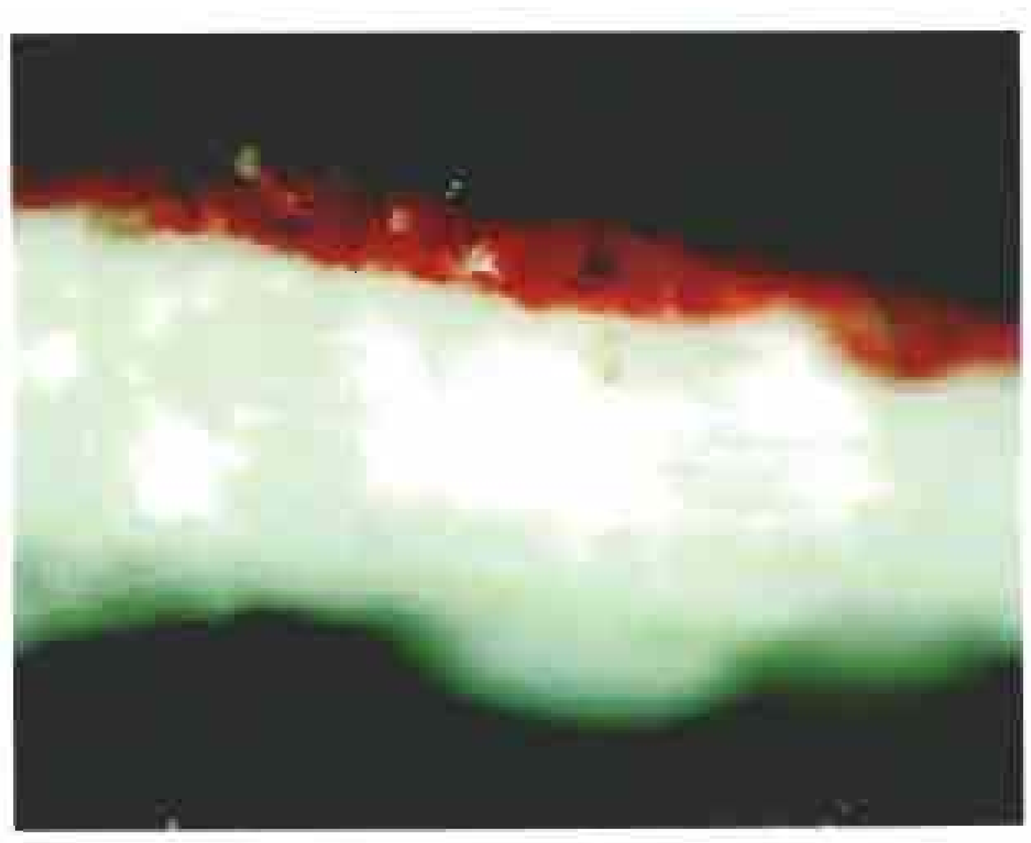
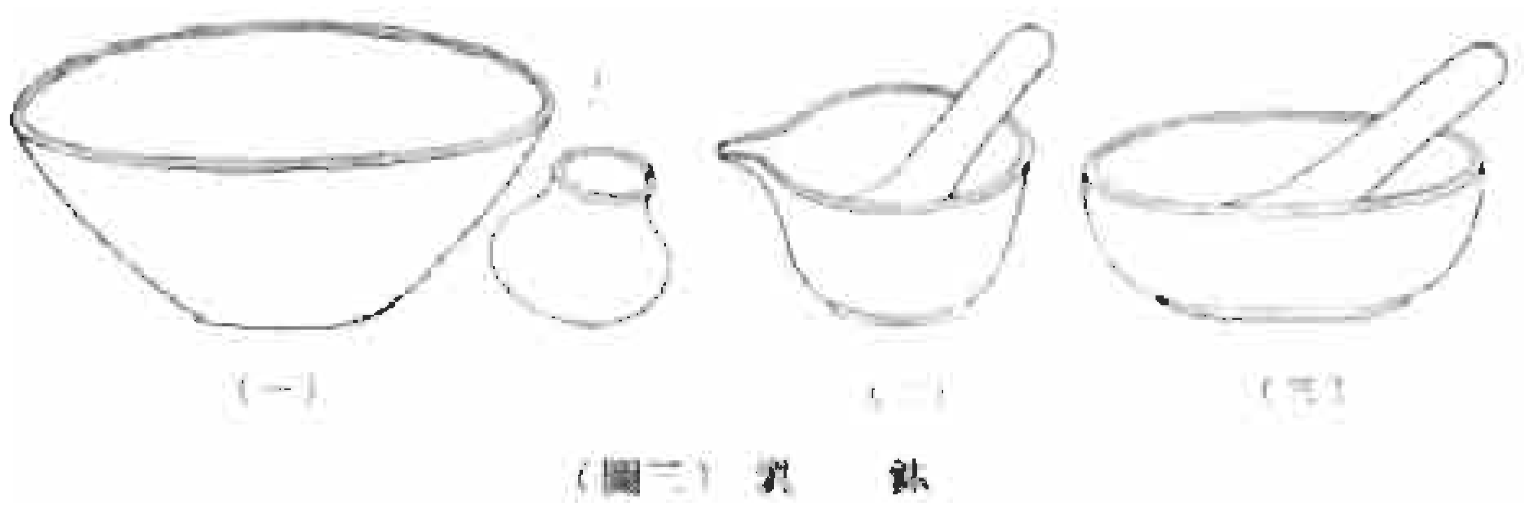


Fig.10 Sample ZH2: it vanished more than once during the preparation of a cross section, due to its dissolving components, magnification 200x

Fig.11 Cross section of sample Zh2, magnification 500x

Fig.12 Cinnabar crystals on a matrix of barite

concocted by the Chinese in a simple refining process, the result of which is called vermilion (Fig.13).



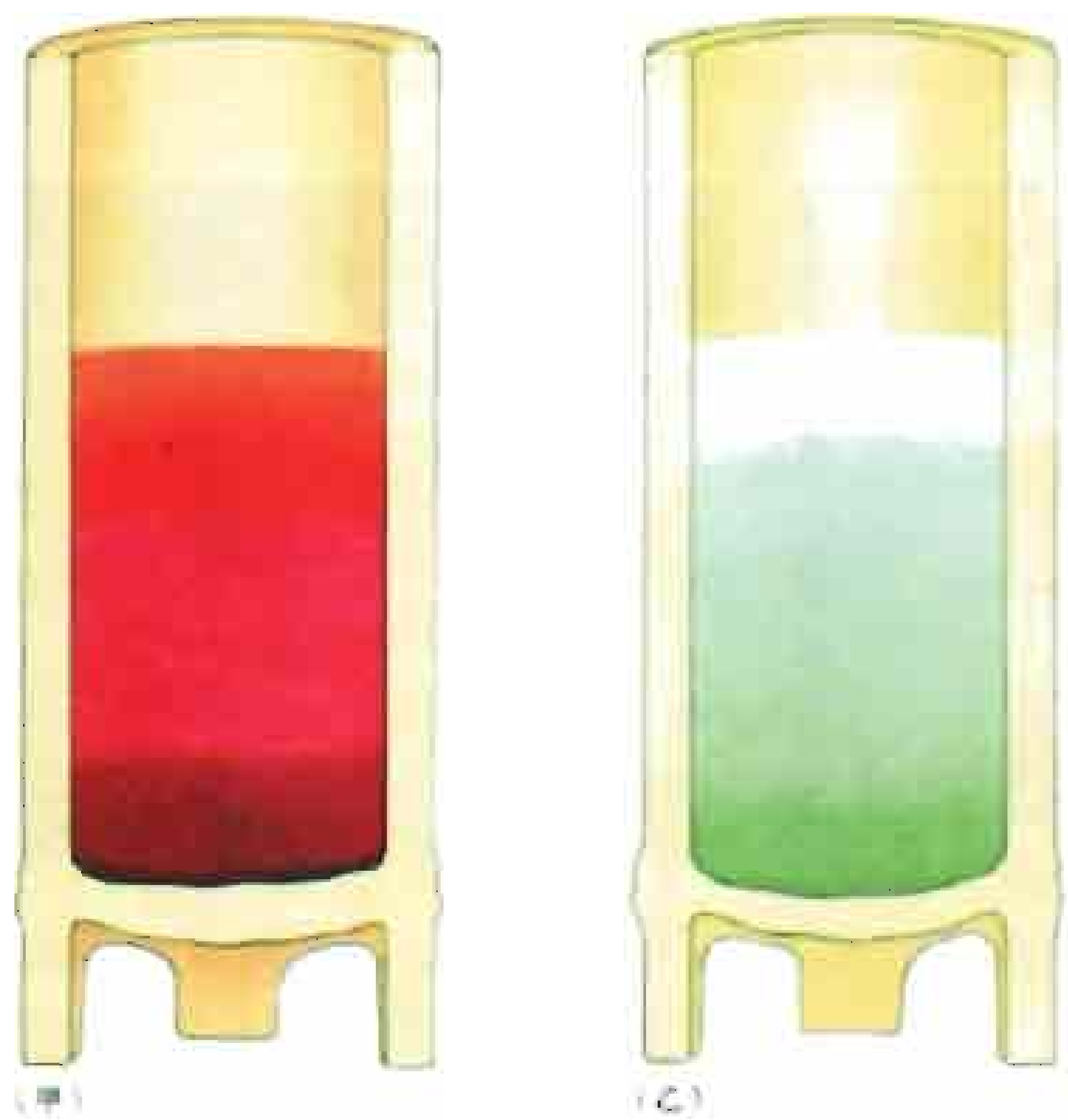


Fig.13 The split bamboo tube with vermilion and malachite separated in three layers: the bottom layers are called 'first red' and 'first green', from Yu Fei'ans book

Yu Fei'an describes the ancient method of preparing cinnabar for the painter's use: "Cinnabar must be ground in a mortar. The finer the grain is grounded the better. Then it is put into a bamboo tube. At the bottom the bamboo tube must be a bit longer than the lowest partition. The tube must be clean and must be bound together using a lead thread to prevent it from splitting open. Use animal glue in the thicker solution and of it only the top clear solution. Mix this together with the cinnabar in the bamboo tube while adding clean water. Let it rest for an hour. Heat the tube au-bain-marie in an earthenware pot over a slow fire. It must not reach to boil therefore you must add cold water every now and then. When the cinnabar in the tube is almost dry, you must let the water cool down. Now wait for the cinnabar in the tube to dry up completely and remove the lead thread from the bamboo tube. Do not let it split by itself, but carefully cut it open with a knife. Now the tube contains a top layer of true red that close to the top will be yellow and this is called third-red: the bottom layer is called first-red and will be purple at the bottom of it: a clear red which is called second-red was in the middle. The three colours: first-red, second-red and third-red are kept separately in different jars[7]. The method described by Yu relies on the process of separating the size of the grains of the mineral into different layers. The coarser the grain, the heavier it is. The slow heating of the tube with the suspension of glue-water and cinnabar will start the process of separation into layers of different size grains, the heavier grains settling down before the finer and therefore lighter grains. This result of layers in different hues was the same as Yu states: the finer the grain the better.

The painting of Fig.14 by Zhao Yong *Horse and Groom* is dated 1347 and is a good example of the use of cinnabar in the dress of the groom and azurite in the rim of the dress.

(3) Azurite and Malachite

The third layer is a whitewash Azurite and malachite are found together and sometimes the one changes into the other -under the influence of water and light-due to a chemical process (Fig.15). The

Fig.14 The painting of Horse and Groom by Zhao Yong, 1347, Acc. No. F1945.32, Freer Gallery of Art. Smithsonian Institution, Washington D.C. (USA)


Fig.15 The location from which sample YD2 was taken


Fig.16 Cross section of sample Yd2, magnification 200x

Fig.17 UV photograph of the cross section of sample YD2, magnification 500x, measure strip of 100 μm

murals of the Qianling tombs show a form of copper green [*Lüyan*, 绿盐] that is closely related to malachite(Fig.16 and 17).

In the Yide tomb this paint layer is identified and confirmed by the X-Ray diffraction that showed 10% silicon and 90% para-atacamite $Cu_2Cl(OH)_3$.

The suspension method of preparation by Yu Fei'an is also used for the preparation of malachite and azurite. The bottom layer always holds the deepest hue and will be called first-red, first-green or first-blue. The coarser the grain, the heavier it is. The slow heating of the tube with the suspension of glue-water and malachite will start the process of separation into layers of different size grains, the heavier grains settling down before the finer and therefore lighter grains. As mentioned before, Yu is convinced that the finer the grain is grounded the better the colour is. But there is a limit to this: The size of grain determines the hue of the colour, and the smaller grains display less colour than the coarser grains, so that if the mineral is ground too finely the colour will disappear altogether, leaving you with nothing more than a whitish powder. This is a problem with malachite and to a lesser degree with cinnabar.

In western grinding techniques, this separation process is done in a different way, using a set of sequential sieves. This European method involves first grinding the mineral, followed by 'wet sieving': putting it through a set of sieves, starting with a coarse-mesh sieve and gradually using a finer and finer mesh that separates the grains by size. This European method provides a regular even sized paint matter. The Chinese sublimation method is less rigid in the separation process, and it is a matter of taste and style wetter one would prefer one result over the other. Currently most Chinese manufacturers of paint use the same sieving method while still selling this as traditional Chinese paint. When I visited the department that prepares the painting materials for the Beijing school of Fine Arts, I noted that they use the wet sieving method for grinding malachite. The same method is used for example at the mill of Kremer pigments in Germany and all over Europe.

Malachite is found in several places in China: it is still mined in Guangdong, in Sichuan, and in the Daye copper mine in Huangshi Hubei. Its connection with copper had already been documented by the Song dynasty. According to Fan Chengda from the Song dynasty in his *Guihai Yuhengzhi* [8]: "Green, west of the You River are places with copper, between the raw ore there are minerals called mineral green. There is also one kind that is as brittle as dry earth, it is called mud green".

Yu Fei'an says that there are four kinds: "...mineral green, malachite, copper green and pebble green. Mineral green is formed in small lumps; the best kind is from Huize, Dongchuan and from Gongshan in Yunnan. The second-best in terms of quality comes from Nandan and Baoyang in Guangxi and it is also found in Iran and Burma. Malachite is formed in lumps, and is by nature composed of light and dark layers. The colour is reminiscent of peacock feathers, and it is frequently used as an inlay in artisan's pieces. Loose pieces and fragments can be used to make a green colour. The material is so hard that it can only with great effort be crushed with a hammer. The pieces must then be ground in a mortar, turning in one direction only. If they are ground in different directions, small balls of the mineral will form and the process cannot be reversed" [9].

Maimai Sze in the *The Mustard-seed Garden Manual of Painting*: " The mineral is so solid it cannot be crushed. Take some earwax and make small balls of it, than you can easily rub it into a paste" [10]. The earwax keeps the mineral in its place so that it stays in the mortar when working on it. Here we also find the method the mineral green must be used and stored: " The glue must not be mixed before the time of use. Use clear glue water in a dish, slowly add water and warm it over a low fire to dissolve the mineral green for use. After use the glue must be removed. There must be no glue left in the paint or it will affect the colour of the green or blue. To skim off the glue, use boiling water, and add it to the blue or green. Put it on au-bain-marie, and make sure no extra water is added; after a short while the glue will float to the top and can be skimmed off. This is called the ' skimming off' of the glue. If this is not done properly, the next time it cannot be used because the green and blue will not be brilliant. Shortly before the next use, new glue must be added" [11].

(4) White pigment

White pigment in various forms is present in the Qianling murals. X-Ray diffraction of samples gave a result of 100% chalk-calcite. One contained 50% chalk-calcite and 50% aragonite-calcite, and another place is made up of 90% chalk-calcite and 10% quartz. Micro chemical testing sometimes left a kaolin residue that cannot be dissolved with the applied acids.

Fig.18 MAK 529: Three kings in a Temple, Rijksmuseum Amsterdam

3 Three kings in a Temple, MAK 529, Rijksmuseum Amsterdam

3.1 Gilding

Fig.18 is The MAK 529: Three kings in a Temple, Rijksmuseum Amsterdam. Questions arise on the kind of gold and the technique and process of application. The cross-section of the sample provides the answer. The cross section shows a gold layer of tiny particles that lay on top of the impasto layer. The gold is restricted to the top layer (Fig.19). Traces of copper are spread in the whole sample, with a stronger concentration of copper in the layer directly under the gold (Fig.20). In the ground layer of this sample we find calcium with traces of sodium and relatively large particles of silicon. Some particles in the ground layer contain aluminium and iron.

To define the nature of the calcium carbonate in the white render layer it has been analysed by X-Ray diffraction. The result did not indicate aragonite but chalk. The impasto has a compact white body mass with an even spread of fine particles. A render layer

Fig.19 MAK 529 rm74-5

Fig.20 MAK 529 rm74-5, dark field

Fig.21 MAK 529 rm74-5, UV light

can be seen, and a thin layer of about 10 μ m with very fine particles at the top. Under normal light, UV and in dark field the render layer is clearly distinct from the white impasto (Fig.21). This might indicate an organic component, most likely glue. On a black and white SEM image the layer looks similar to the impasto layer and cannot be defined by size or structure of the particles.

3.2 Gold

Analysis of the top layer provides evidence of gold in a very specific form: milk gold, (*rujin* 乳金). Milk gold is a typical Chinese form of preparing gold in gilding. This method differs from the most commonly known method that is used all over the world: gilding with gold leaf. According to Yu Fei'an, milk gold is prepared by painters. They take a small part of gold leaf and rub this between thumb and index finger together with glue until it is ready to be used as paint.

There is a recipe in a Chinese painting that describes the preparation of material for the impasto. "The most important traditional material consists of talcum powder, animal bone glue, and a fixed amount of tong oil to prevent cracking of the mass. Currently milk glue (*rujiao*.乳胶) is mostly used. Milk glue is an emulsion of talcum powder and glue without the traditional additive tong oil. The Tong oil is left out to prevent problems with the temperature of the glue. When lines are wide the mass must be thick, and for finer lining the mass must be thinner. The mass should be stand on the surface without any flowing" [12].

3.3 Lead

Lead is significant in two different forms: lead white and yellow lead. A third form of lead is red lead, was not found. Red lead is commonly used as a red pigment in China (Fig.22). Under the rim of the yellow robe of the left figure the white render layer contains calcium carbonate with traces of manganese and silicon. This could point to the use of a talcum rich material. Although this area of the fragment has no

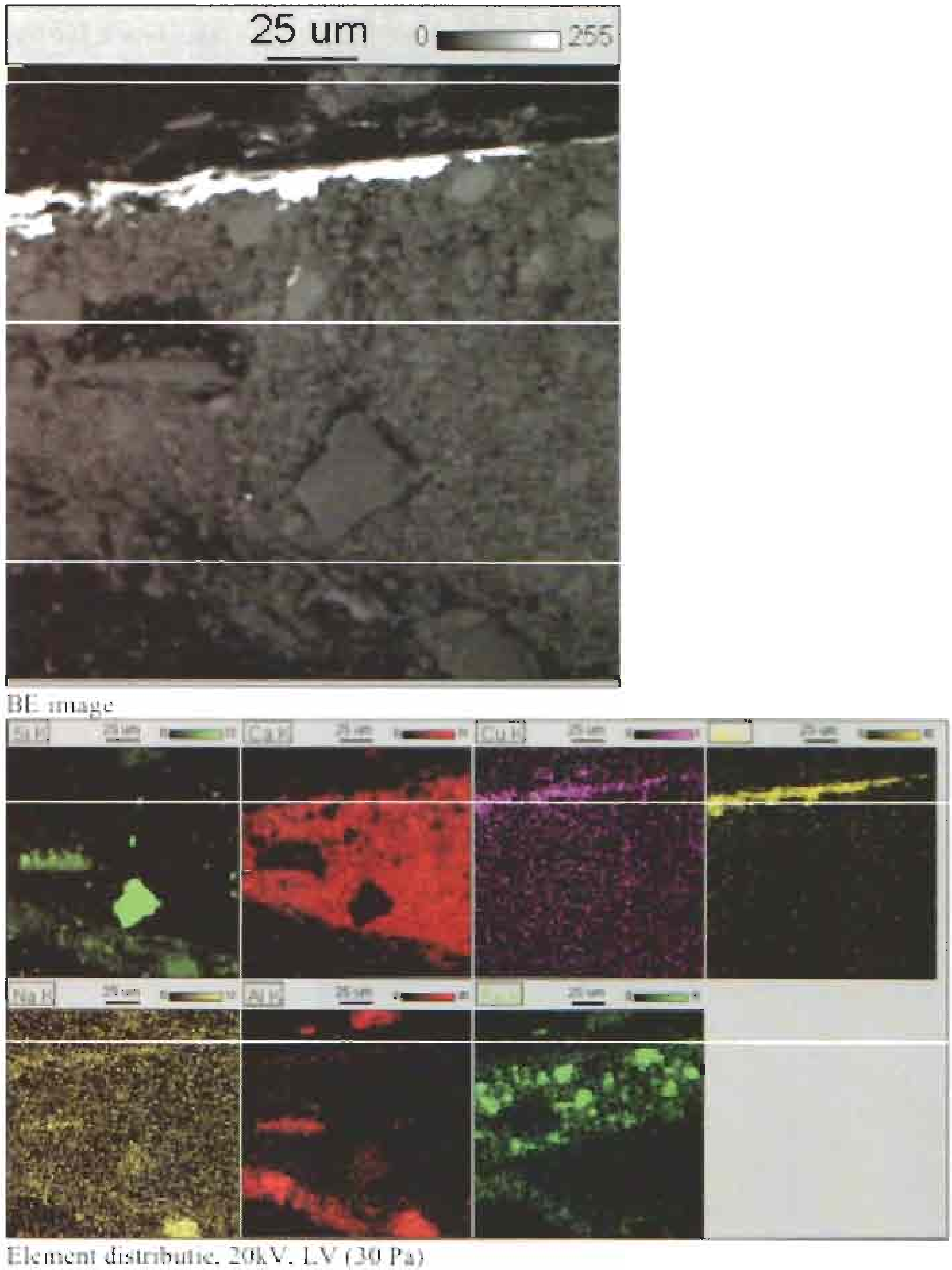


Fig.22 MAK 529 rm74-5 SEM image and element distribution

impasto, the composition of the material fits the description in the recipe for ' impasto under gilding' . In many places in China a variety of talcum rich minerals are found. This sample was to small to perform further tests for tong oil that was mentioned in the recipe. The lead yellow in the top layer might be the reason for this specific use of a talcum rich material in the render layer.

The top paint layer contains lead, copper and traces of phosphor, a combination results in a soft yellow colour. It is feasible that the colour has faded over the years. This type of yellow is locally known as yellow layer (*huangqian*黄钱) a term commonly used for lead monoxide, litharge or massicot.

The white wainscot behind the figures also contains lead white. According to Yu Fei'an "Red lead is the same as yellow lead, which is also called Zhang red. There are two shades of lead used in murals, one is deep and one is pale. Lead white is often confused with gaoling or white chalk. The one which has turned black after you mix it with vermilion or red lead, is lead white" [13].

The top paint layer in this sample is also white (Fig.23). This is a fine example of lead white (*baiqian*, 白钱). This material has been used in China as a white colour since the early recorded history. The render layer of the sample is largely made of calcium, aluminium and magnesium with small traces of iron, boron, sulphur and arsenic. The components are consistent with kaolin (*gaoling* 高岭土). On the back of the robe, a semi transparent render layer between the yellow earth ground layer and the paint layer was found. This layer turns out to be common feldspar. Small traces of phosphor and sulphur indicate the presence of bone ash in this

Fig.23 MAK 529 rm74-5 paint and lead white

render layer. Under the microscope we see small fibres in the yellow earth layer, likely to be hemp chaff. Further analysis is impossible in view of the minimal amount of material in the sample. The white render layer again consists of calcium with traces of magnesium. The thin top layer is an iron containing paint: red earth or haematite (*chitiekuang*, 赤铁矿), which is commonly used as a red pigment in China.

3.4 Clam white

The last type of white is Clam white (*Gefen or Hafen*, 蛤粉). In the Yi De tomb, the mixture of 50 % chalk and 50 % aragonite was founded. Aragonite is a form of calcium carbonate that occurs in corals, pearl and shells. In Chinese painting, there is a special white called *gefen*. The most commonly used translation for *Gefen* is oyster white, which leads to a misunderstanding of the nature of *Gefen*. Although the material is white and made of a shell, it is not made of oysters. To complicate the issue even more, there is actually a material called oyster white, which is made of oyster shells and is used in building as a mortar, in the same way as the lime that is made by burning stones. It is also mixed with tong oil for use as a whitewash for ships.

In the book " Chinese Technology in the Seventeenth Century" written in the seventeenth century by Song Yingxing, the difference between oyster white and clam white is made clear: "Some people mistake clam shell powder for oyster lime. This is because they have never troubled themselves to learn the nature of things" [14].

3.5 Oyster or Clam

It is possible that in some periods painters used oyster white instead of clam white. Oyster white is obtained by burning old oyster beds [*lifang in Chinese*, 蛎房] along the seacoast. The burning process involving charcoal turns it into a lime that is ready for use. Chemically clam white and oyster white are the same: calcium carbonate CaCO white is obtained by burning old oyster beds along the seacoast. The burning process involving charcoal turns it into a lime that is ready for use. Chemically clam white and oyster white are the same: calcium carbonate $CaCO_3$. The difference can, however, be shown by XRD, since oyster white contains only a little aragonite, while clam white is almost 100% aragonite. In the impasto lines on statues of the *Shui Lu An* the use of clam white is proven by the XRD.

This makes me wonder about the availability of this material, since the gilded lines are obviously overlaid with gold: there is no visual reason for *Gefen* to be used in this particular example. There might, however, be a structural reason: the lines are laid onto and are in relief on the statue. It may well be that this substance provides a smoother or denser base than others and therefore is easier to use for the haute relief lines of the gilding, or it may be that the gold attaches to this lime particularly well. However, often the availability of a material is the best reason for use. The local shellfish that was used for food leaves probably leaves heaps of shells ready for burning and grinding this *gefen*.

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中国壁画颜料成分组成的探讨

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摘要：中国壁画颜料的成分很复杂，应用历史也很长，唐代乾陵壁画是中国壁画技术应用的里程碑。本文研究源于三个公元8世纪的壁画，比较了中国古文中有关矿物颜料与植物染料的描述。当我致力于搞清各种颜料名称及成分时，我遇到了很大的困难，大量的颜料名称混杂不易辩别矿物颜料和有机颜料。

壁画中大量应用的是本地产的矿物颜料，如：朱砂、赤土、孔雀石、蓝铜矿、雄黄、雌黄、高岭土、白垩土等。除了已知的矿物颜料和名称外，还有一些未确定的成分，如云母，很少在艺术史书籍中提及。

壁画研究中最少涉入的领域是植物染料的应用，我认为植物染料是一种真正的壁画颜料，公元五世纪的书籍“起名要素”就是一个佐证。最重要的是，我从几种例子中发现了证据，就是植物成分与其它植物染料或矿物颜料混合应用在壁画中

本文希望能促进人们对不同物质在各种环境中习性的认识和了解，以期对保护实践活动有所帮助。我希望对壁画材料提一点自己的看法。

关键词：问题；中国壁画；矿物颜料及植物颜料

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ISSN 1000-7954
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