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第一章 壁画保护

"Australia-China Collaboration on the Art History, Restoration and Conservation Study of Mural Paintings"

澳中两国有关壁画艺术史，修复与保护研究的合作

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Abstract

This paper reports on the conservation and materials analysis of two tomb mural programs excavated by Shaanxi Provincial Institute of Archaeology in 2014, from the Tang dynasty (618-907) and Yuan dynasty (1271–1368). The characterisation of the historic Chinese Tang dynasty murals, examined the painting materials, artistic practices and compatible conservation approaches as part of a long-term collaboration with Shaanxi Provincial Institute of Archaeology, China and The University of Melbourne, Australia. In addition to investigating the earth based pigments of iron oxide red, iron oxide yellow and malachite with Handheld XRF and Inductively Coupled Plasma Optical Emission spectroscopy, the study focused on the presence or absence of binding materials. Given that only stable mineral based pigments can be embedded in a calcium hydroxide (Ca(OH)2 plaster layer for a true fresco technique, and pH sensitive pigments are mixed with a binder in the secco technique, areas coloured with pH sensitive pigments were investigated. Paint samples in green coloured areas assumed to be azurite or malachite with inorganic analysis, were subsequently analysed with Synchrotron Radiation Fourier Transformer Infrared (FTIR) Microscopy at the Australian Synchrotron. Examination of the porous paint cross sections with micro FTIR in Attenuated Total Reflectance mode aimed to assess the spatial distribution of compounds across the mural samples and identification of low concentrations of binders that are possibly present in the secco layers, with results pending. Complementing this study was the production of historically correct reconstructions to test assumptions, material analysis protocols and degradation pathways.

Key words

Conservation, China, cultural materials, mural painting, research collaboration

摘　要

本文对2014年陕西省考古研究所发掘的唐代(618 — 907)和元代(1271 — 1368)墓室两幅壁画的保存与材料进行了分析。作为与中国陕西省考古研究所和澳大利亚墨尔本大学长期合作的一部分，通过对中国唐代历史壁画的特征描述，研究了绘画材料、艺术实践和兼容的保护方法。除了用手持XRF（X射线荧光）和电感耦合等离子发射光谱技术研究氧化铁红、氧化铁黄和孔雀石的颜料外，研究的重点是粘合剂的存在与否。考虑到只有稳定的矿物基颜料才能被嵌入到氢氧化钙［Ca(OH)2］石膏层里，用于真正的湿壁画技术中，在干壁画技术中，将pH敏感颜料与粘结剂混合，研究了pH敏感颜料的着色区域。用无机分析假定在绿色区域的绘画样本是蓝铜矿或孔雀石，随后在澳大利亚同步加速器上用同步辐射傅立叶变压器红外（FTIR）显微镜进行分析。用微红外光谱在衰减全反射模式下对多孔涂料截面进行检测，目的是评估化合物在壁画样本上的空间分布，以及识别可能存在于干壁画层中的低浓度粘合剂，结果有待研究。这一补充研究，是历史上正确重建的产物，用于测试假设，材料分析协议和降解途径。

关键词

保护；中国；文化材料；壁画；合作研究

The collaboration

In 2014,a collaborative team of experts from Shaanxi and Henan Provinces China and Victoria Australia was established. Three formal agreements for academic cooperation were signed between the University of Melbourne (UoM) with the Shaanxi Provincial Institute of Archaeology (SPIA), the Henan Provincial Administration of Cultural Heritage (HPACH) and Zhengzhou University (ZZU). It was agreed that the SPIA–UoM cooperation would focus on mural painting in Shaanxi Province. A report to the Second Qujiang Forum in 2015 outlined the establishment phase of this research and this Australia-China collaboration has now completed its third year under the current five-year agreements.

With a focus on the technical study and scientific analysis of tomb mural painting in Shaanxi Province,

Figure 1 Mural painting of a phoenix, Tang dynasty (618–907) tomb M68, Taipingbao site, Jinyang County, Shaanxi Province. Photo: SPIA.

Figure 2 Mural painting scene of wine preparation, Yuan dynasty (1271–1368) tomb, Luogetai, Hengshan County, Shaanxi Province. Photo: SPIA.

partners selected a multi-disciplinary team of art historians, scientist materials conservators and archaeologists to establish a research training and knowledge transfer program. In annual visits between Xi'an, China and Melbourne, Australia, by experts and graduate students, the joint team continues the direct examination of mural paintings in situ at field sites, museums and institute collections. Cultural materials conservation research and the study of treatments is supported by lectures, documentary film making and screenings, and an internship program. In 2015 SPIA hosted two UoM Grimwade Centre for Conservation Materials Conservation internships at the mural conservation laboratories of the Xi'an Qujiang Museum of Fine Arts working under leading SPIA mural painting conservator Mr Wang Xiaoxiao. The interns worked on two mural paintings excavated from the Yuan dynasty tomb in Hengshan County, Shanbei region of Shaanxi Province.

Aims and activities

The broad aim of the UoM-SPIA joint research project is to understand historical wall painting materials, artistic practices and conservation methods. The particular focus is Tang dynasty tomb mural painting, due to their quality and the importance of discoveries in Shaanxi Province, although comparative studies are being considered such as the earliest mural paintings at Shimao stone city (2,000 BCE) in the long term. Untreated mural paint samples of pigmented areas, grounds and support layers were collected from archaeological sites by SPIA and brought to Melbourne for analysis in 2016.

The Tang dynasty (618-907) samples from tomb M68 discovered in 2014 at the Taipingbao site, Jingyang County, Xianyang (to the north of Xi'an city) in Shaanxi Province were analysed in detail. Although the identity of the tomb occupant is not known, this tomb was of exceptionally high status with (originally) a spirit road leading to the tomb's colossal 30m diameter rammed earth mound. Underground, the tomb was large, extending 35m in length and 10m in depth with a long entry passage, five side niches for the storage of burial goods, five ventilation shafts and a single coffin chamber. Surviving mural paintings on the tomb passage walls indicate an extravagant pictorial program including guards with halberds, a male civil official and an attendant woman, two Indian Buddhist monks, a horse and groom, a riderless horse and three directional animals – dragon, tiger and phoenix. The murals are bright, richly coloured and skilfully painted in a lively style indicative of a date in the first half of the 8th century.

The Yuan dynasty (1271-1368) mural paintings were from a tomb discovered in

2014 in Luogetai Village in Hengshan County in north Shaanxi Province. This stone tomb is significant for its complex scheme of painted murals covering plaster-lined walls. The tomb has a rectangular entrance room and an octagonal chamber with a domed roof. The whole tomb is 6.1m long and 2.8m high with a 2.3m diameter dome. The tomb chamber's mural scheme comprises celestial scenes in the upper register, images of the tomb owner surrounded by scenes of filial piety in the middle and scenes of earthly pleasures such as wine and tea preparation, and musical performance in the lower register. In Xi'an during 2015, the Grimwade Centre intern master degree students worked on a scene depicting wine preparation from the Luogetai tomb under supervision of SPIA experts. This included material testing and conservation treatment of this section of the mural painting scheme.

Laboratory analysis

Information on the original materials assists in determining the original artistic practices used in the production of wall paintings. Discussions with Shaanxi-based wall painting conservators and observations of conserved and treated wall paintings in museums, suggested that the Shaanxi mural paintings may be fresco with secco additions. As such, the joint team planned analysis of the untreated plaster and pigment layers samples. In situ analysis by SPIA with non-invasive techniques including infrared examination, Raman spectroscopy and Handheld X-ray fluorescence (XRF) detected these key elements: calcium, copper, iron and lead.

At the Grimwade Centre, an initial focus of laboratory work was on the elemental identification and quantification of elements in the mural paintings from the Tang dynasty Taipingbao tomb and Yuan Dynasty Luogetai tomb, as well as other comparative mural fragments from Shaanxi Province and contemporary reference samples. The following methods of testing were used: Handheld X-ray fluorescence (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES) and Fourier Transform Infrared Microscopy (FTIR). In developing the analytical protocol, reference samples of pigments of Chinese origin that are commonly used today in the restoration of historical mural paintings, were also studied. This set was useful in developing material profiles and identifying areas of restorations or non-original material.

For inorganic analysis, Handheld XRF is a non-destructive technique for identifying mineral pigments and mineral supports. It is a useful characterization as a first step; for example, it can detect the presence of iron to potentially indicate iron based pigments from the mural's paint layer or the surrounding earth. ICP-OES then builds on this elemental identification by providing quantitative data in parts per million (ppm). This information characterizes pigments more accurately as their relative ratios in ppm can be compared to the elemental composition of pigments and their identification. Higher levels of iron than those expected for an iron oxide pigment may consequently indicate iron sourced from the surrounding earth. For organic analysis, FTIR examined the organic components such as binders, additions to plaster and support layers and organic colorants. Often such materials are included in small quantities and trace organic components are difficult to detect. To test the theory, model samples were made up by UoM master degree minor thesis students and analysed using the same protocols to ensure detection levels were as expected for the known model samples.

Table. Summary of inorganic analysis of pigments and mineral support layers:

This table provides a summary of the key elements and their quantities identified in the Taipingbao tomb mural samples. Calcium was detected using XRF in all samples. The presence of strontium peaks associated with a marine source of calcium suggests a calcium carbonate support. This implies a fresco material and therefore, technique. It should be noted that Ca levels diminish in the earthen support layer in support of this assertion. For the black painted areas, although these are likely to be carbon black, XRF and ICP-OES were unable to detected carbon. The red paint sample TP-1b, however included the presence of iron at higher levels compared to the other paint samples tested, suggesting its significance and the possibility of iron oxide, a pigment consistent with fresco materials and techniques. For sample TP-6, the relatively higher levels of iron detected second only to the earth support layer, may also be indicative of an iron

Fragment	Sampled	XRF analysis	ICP-OES analysis (mg/L)
Paint layer			
TP- 1a	Black	Ca	Ca 1498.812
TP-1b	Red	Ca and Fe	Ca 633.682,Fe 20.175
TP-1c*	Green	Ca and Cu	Ca 641.345, Cu 13.987
TP-1d*	Orange	Ca and Fe	Ca 1216.603, Fe 11.714
Support layer			
TP-2	Plaster surface	Ca and Fe	Ca 712.940, Fe 8.031
TP-6	Red	Ca and Fe	Ca 485.216, Fe 26.790
TP-6	Plaster	Ca and Fe	Ca 748.191, Fe 9.912
TP-6	Earth	Ca and Fe	Ca 177.631, Fe 98.977

oxide pigment. While copper was present in green painted area TP-1c, copper was not detected in any other samples, and suggests the presence of a copper based pigment. The use of copper pigment is inconsistent with a fresco palette and therefore is of particular interest, as this is the area where binder is most likely to be present and where organic analysis should focus. For the orange paint layer, TP-1d, iron was detected at lower levels than in the red suggesting the inclusion of less iron oxide. However, if we observe the TP-6 sample of the plaster surface and plaster, the concentration of iron detected using ICP-OES is comparable, and iron oxide may not be a fingerprint for the orange area. While examination of the smaller XRF peaks indicated the presence of lead in this sample. Lead is also detected in association with green and confirmed with ICP-OES (although not listed in the table), however was not at significant levels. One explanation is that both of these pigments may be applied as a secco and lead may be added to improve working performance of the paint. Further analysis, however is required to confirm this hypothesis and may provide an insight into a diagnostic painting technique.

Model pigment samples

As noted earlier, to understand the behaviour of fresco and secco materials in mural paintings over time and the analytical protocols, model pigment samples were created. Tang murals have historically been constructed with binders such as peach gum, dammar, gelatin, mastic, rabbit skin glue, sturgeon glue, egg, asparagus paste, casein from various animals and hide glue from various animals. This provides a range of possibilities for model samples to characterize the behaviour of true fresco materials and technique versus a secco (with binder) techniques. Given our enquiry into the possible use of binders in the secco areas of alkali sensitive copper based green pigments, model samples focused on this aspect of the study and the testing of peach gum, animal hide and tempera (egg). The study characterized the response of Tang-like organic and inorganic materials in these binders to accelerated aging by means of increased temperatures of x oC, and at increased temperatures of x oC together with a higher relative humidity of 70%. Samples were analysed using visual analysis, chemical spot tests, Ultraviolet (UV) fluorescence, FTIR ATR and Handheld XRF. In such accelerated aging conditions, it aimed to identify the key markers for the binding materials, examine any changes to the organic binders used in fresco or secco techniques, and their detection levels.

This test focused on malachite (copper based) and haematite (iron based), as these are diagnostic and commonly used colourants used in wall painting technique. Moisture rich bricks were coated with calcium carbonate, followed by the pigment alone and the binders combined with the selected pigments. Controlled accelerated aging was undertaken over six months to identify degradation pathways at higher temperatures and at higher temperatures in a moisture rich context to simulate a burial environment similar to the conditions of Chinese tomb murals. FTIR ATR analysis was unable to detect the binder in the samples, despite their inclusion in the model samples and contrary to UV fluorescence and chemical spot tests indicating the presence of a binder on half the samples. This was in part due to the strong overshadowing band between 1300 to 1500 cm-1

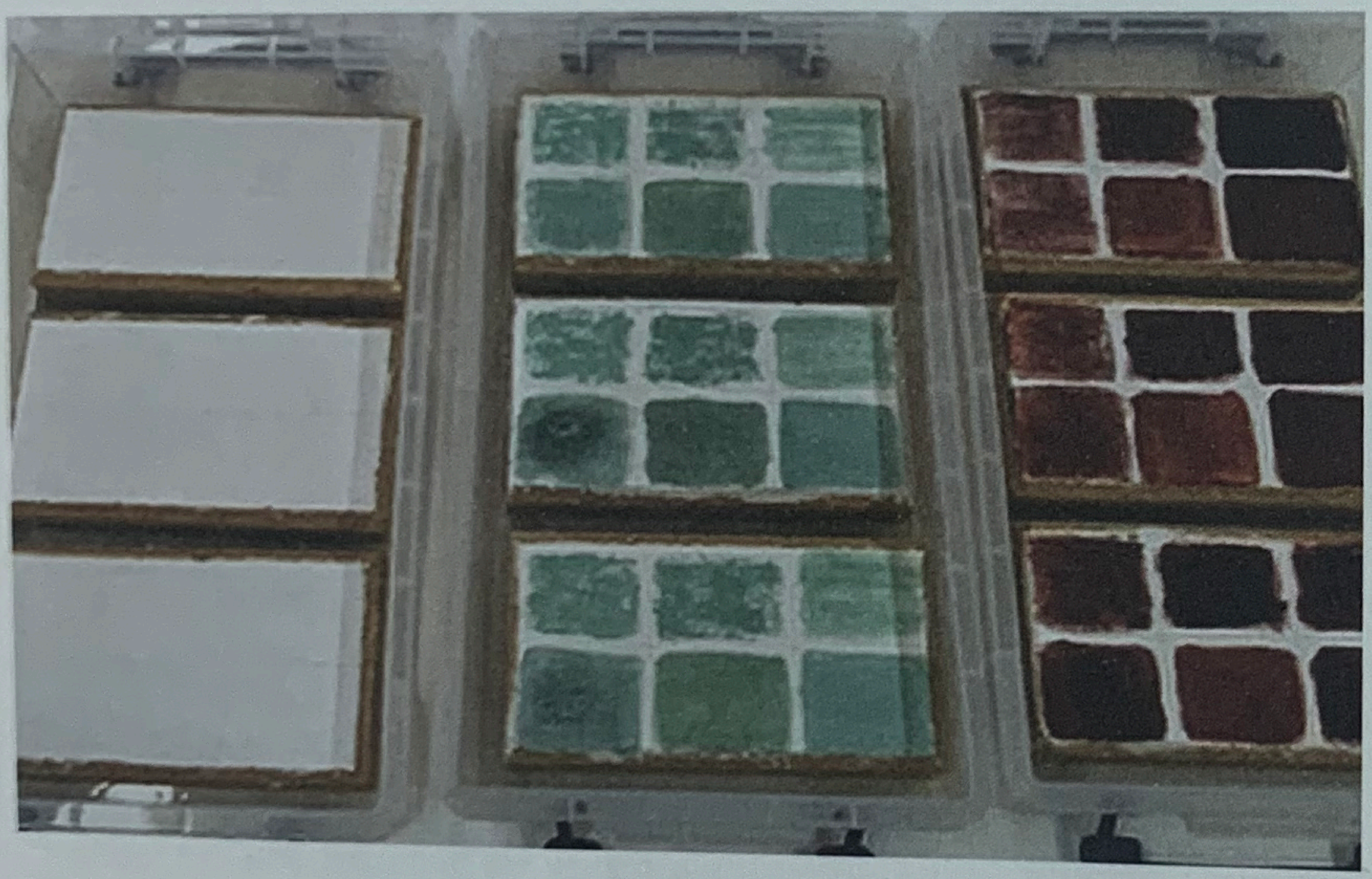

Figure 3 Model replicas of fresco supports with malachite and iron oxide also applied in the secco technique with peach glue, animal hide and tempera. Photo: UoM

from C-O stretching from the carbonate pigments that masks a signal for the protein binders. This is a common limitation of FTIR ATR analysis as well as the poor signal to noise ratio. The results also showed the rapid absorption of the binders into the substrate of the calcium carbonate support. While handheld XRF analysis clearly identified the known inorganic pigments in the model samples. Overall such analysis with the aged model samples showed the limitations of FTIR ATR in either identifying the binding materials highlighting the need for higher resolution techniques, or that the binder had partly been degraded through the accelerated aging process.

Synchrotron Radiation FTIR microscopy at the Australian Synchrotron

To address the limitation of successfully identifying binding materials in wall paintings, the UoM-SPIA team received a grant from Australian Synchrotron to undertake analysis of 'Two Chinese Mural Paintings from the Tang Dynasty (618-907) and Yuan Dynasty (1279-1368): Characterizing their binders and pigments',using the two sample sets – from Taipingbao and Luogetai.

A Synchrotron is a large analytical instrument about the size of a football field that accelerates electrons to almost the speed of light. As the electrons are deflected through magnetic fields they create extremely bright light. The light is channeled down different beamlines to determine particular material properties. The benefits of Synchrotron Radiation (SR) are its high sensitivity, and its qualitative and quantitative information permitting detailed analysis. SR IR microscopy is able to produce spectra at a very high spatial resolution at 5μm made possible by the SR source. When compared to conventional IR, the spatial resolution is ten times more at 50μm, highlighting its limitation in detecting materials at smaller quantities in a paint matrix.

Samples analysed from the Taipingbao and Luogetai murals included a range of pigments, grounds and earthen sections, as well as layered mural painting structures. These cross-section paint samples were embedded polyester resin, attached to an aluminium block and then micro-tomed to produce a flat surface for analysis in ATR mode.

Although our final results are forthcoming, preliminary data analysis on the green sample from the Tang dynasty mural fragment from tomb M68, Taipingbao Village is presented (Figure 5). Analysis of the spectral map with OPUS 7 showed two peak integrations. One peak integration centred at 1735cm-1 corresponds with a carbonyl peak that partly coincides with the green pigmented. This may suggest the presence of a binder, however much further analysis of the other samples needs to be undertaken to make such conclusions. Another peak integration at 1554-1321 cm-1 centering on the 1419 cm-1 peak, is characteristic of calcium carbonate and is distributed throughout

Figure 4 The UoM–SPIA team at Australian Synchrotron in 2017. Photo: UoM

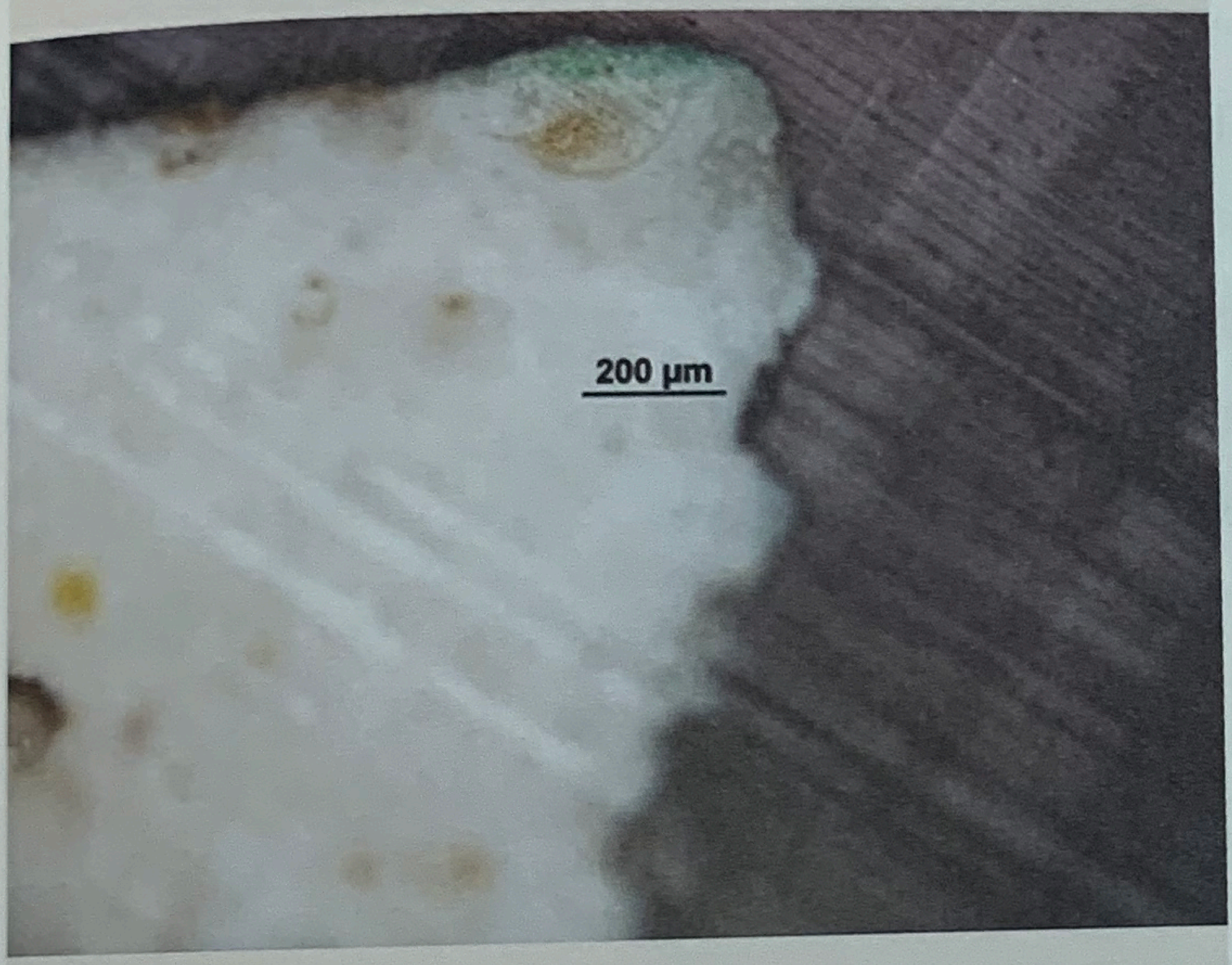

Figure 5 Sample of M68, Taipingbao Village, Tang Dynasty (618–907) after SR IR ATR analysis of 51 x 10 points at the upper green pigmented area on a calcium carbonate ground. Photo: UoM

the layer. This corresponds to our earlier results and knowledge through analysis of the Taipingbao tomb murals.

Preliminary studies and analysis by the joint UoM-SPIA team are increasing our understanding of mural paintings in Shaanxi Province. Working together develops our methods and strengthens our interpretations through sound collaborations. In this paper we have identified the iron and copper based pigments with handheld XRF and ICP-OES, and the limits of FTIR ATR in characterising binding materials. This was further corroborated from the results obtained by the model samples, which initiated the use of the SR FTIR microscopy as a high-resolution technique with the 5µm spatial distribution to identify smaller components. Results from the SR FTIR microscopy are forthcoming.

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We wish to thank the then minor thesis students, Lexi Maller, Robyn Ho and Madeleine Roberts, of the Masters in Cultural Materials Conservation Program at the University of Melbourne, for their contributions to the project.

Instrumentation

Handheld X ray Fluorescence

A Bruker Tracer III-SD (Rhodium X-ray tube) and S1PXRF software was used for handheld XRF. All samples were gauged at 40keV-10ua, and each sample took sixty seconds to analyse. Peaks were labelled, and the K and L shells were prioritised for diagnostic purposes.

Fourier Transform Infrared (FTIR) with Attenuated Total Reflectance (ATR)

IR spectra was collected with a Bruker Alpha- FTIR spectrometer equipped with a diamond ATR window (Bruker Optik GmbH, Ettlingen, Germany). All spectra were recorded in a spectral range of 4000-400 cm-1 with 256 co-added scans at the spectral resolution of 4 cm-1 resolution and all data was processed with Opus (version 6) software.

ICP OES

Before analysis, samples were prepared following a cold and hot digestion protocol with Reverse Aqua Regia (3HNO3 :1HCl). Samples were compared to a series of standard ionic solutions that contain the elements of research interest, and the digestion completed with the addition of hydrogen peroxide (H2O2). A Perkin Elmer Optima dv8300 & dv4300 ICP-OES instrument was used at a temperature of 8000°C with argon to thermally excite the elements and collect their respective spectral profiles with the spectrophotometer. Calibration curves were produced to detect the concentration of particular element(s).

Synchrotron Radiation (SR) Fourier Transform Infrared (FTIR) Microspectroscopy

SR µFTIR was performed using a Bruker Hyperion 2000 microscope in conjunction with a Vertex 80v FTIR spectrometer fitted with a liquid-nitrogen cooled MCT detector and using the IR beamline of the Australian Synchrotron as the radiation source. Samples were embedded in polyester resin and micro-tomed to produce flat surface for analysis in Attenuated Total Reflectance mode (ATR) with a Ge-ATR crystal. IR was collected in transmission mode with 5 x 5 micron aperture at 5 micron steps following custom defined grid positions. Spectra are the sum of 32 scans at a resolution of 4cm-1. Datasets and peak integrations were analysed with OPUS® 7.0.

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