The Polychromy of Antique Sculptures and the Terracotta Army of the First Chinese Emperor
The Polychromy of Antique Sculptures
Wu Yongqi · Zhang Tinghao
Michael Petzet · Erwin Emmerling · Catharina Blänsdorf (Eds.)
吴永琪·张廷皓·佩策特·艾默林·布勒斯多福 (主编)

The Polychromy of Antique Sculptures and the Terracotta Army of the First Chinese Emperor
古代雕塑彩绘和秦始皇兵马俑

Studies on Materials, Painting Techniques and Conservation
材料、绘画技术和保护之研究

International Conference in Xi’an,
Shaanxi History Museum March 22-28, 1999
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Terracotta Warriors and Horses, Lintong
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慕尼黑巴伐利亚州文物保护局

MONUMENTS AND SITES
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Front Cover: Greek terracotta, about 260 BC, Staatliche Antikensammlungen München, NI727 (photographer: Christa Koppermann)
– three warrior heads with polychromy (photo: Bayerisches Landesamt für Denkmalpflege)

Back Cover: Head of Terracotta Warrior with consolidated polychromy (photographer: Laboratory of the Museum of the Terracotta Army
and Bayerisches Landesamt für Denkmalpflege, Siegfried Scheder)

封面：古希腊陶俑，约公元前260年，慕尼黑国家古希腊罗马艺术收藏馆，NI727（摄影：克里斯塔·克佩曼）
– 三个带彩绘的秦俑头像（摄影：巴伐利亚州文物保护局）
封面：保护后的带彩绘的秦俑头像（摄影：秦俑馆保管部实验室和巴伐利亚州文物保护局）

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Preface

An international Symposium on "Polychromy of the Terracotta Army of the First Chinese Emperor Qin Shihuangdi, Studies on the Polychromy of Antique Sculptures; Materials, Painting Techniques and Conservation" was held at the Historical Museum of the Shaanxi Province in March, 1999. This was the first congress ever held on the polychromy of antique sculptures in the People's Republic of China. Polychromy of antique sculptures has, of course, been one of the central topics of discussion of archaeologists since the 19th century and has influenced contemporary European art into the 20th Century. Intense original colouring cannot be found on a single antique Greek sculpture. Partially due to diverse influences over the centuries, partially due to the deliberate removal of existant colouring, the general public sees sculpture as monochromatic - either white or material-based in colour, even though current research proves it to have been otherwise. The state of information regarding Near Eastern cultures, Egyptian sculpture and Etruscan plastic art is similar to that which has been passed down to us on antique Greek sculpture: at an absolute minimum, fragments or shadowy traces of colour give us a vague idea of the artistic quality and original wealth of the polychromy on antique sculptures.

Thousands of terracotta figures, some life-size, some only a few centimetres high, have been excavated in China in the last twenty years. Almost all of these sculptures are elaborately painted; a large number of these figures have been preserved with their original colouring. Without a doubt the most spectacular discovery has been the tomb of the First Chinese Emperor, Qin Shihuangdi. Not only the internationally renowned Terracotta Army of the emperor, but also numerous other burial offerings are completely coloured. These realistically and intensively coloured figures give us the impression of a striking presence and power previously unknown in antique sculpture.

The papers presented at this Symposium cover not only Chinese excavations, but also examples from Egypt, the Near East and Europe. Questions concerning clothing and textiles as well as aspects of colour symbolism and the meaning of colour in different cultures were examined. And last but not least, painting techniques, materials and conservation problems in the different cultures, with concentration on the aspects of natural science and conservation, were presented.

Compiled in this publication are the revised papers presented at the Symposium; a general view, and a survey on the polychromy of ancient sculpture. It is exciting to pursue the similarities and differences to be found in the finishing of sculptures in the early advanced civilisations. Parallel uses of the colour blue are particularly notable, thus supporting the presumption of an intense cultural exchange in antiquity.

The organisers of this Symposium - notably the Museum of the Terracotta Warriors and Horses, the Department of Historical Monuments, and ICOMOS - hope that the research on the polychromy of antique sculptures and the cultural exchange will continue.

We thank all Speakers for their papers and all participants in the Symposium for their interest and contributions. We would also like to thank Dr. Chen Ganglin, who edited the Chinese papers for the publication. Dr. Irene Helmreich-Schoeller proofed the English translations. Special thanks to Diplom-Restauratorin Catharina Blaendsdorf who, together with the colleagues from the Museum of the Terracotta Army, Mr. Prof. Guo Baofa, Mr. Zhao Kun and Mr. Xia Yin prepared and organised the Symposium.

Dr. Egon Johannes Greipl
General Curator
Bavarian State Department of Historical Monuments

Prof. Dr. Michael Petzet
President of ICOMOS

Director Wu Yongqi
Museum of the Terracotta Army Lintong

Minister Zhang Tinghao
Ministry for the Protection of Cultural Assets,
Provinz Shaanxi
1999 年 3 月，以“秦俑及彩绘文物研究保护”为主题的国际学术研讨会在中囯古都西安举行。这是第一次在中华人民共和国进行的古代彩绘文物的专题讨论会。自 19 世纪以来，古代雕塑彩绘一直是考古学领域探讨的一个中心课题，它也对 19 和 20 世纪欧洲的艺术创作有很大影响。两千年来，由于受到各种因素的影响，特别是许多文物上尚存颜色被人为有意除去，结果今天已无一座保留当初色彩的古希腊大理石雕刻留存世间。虽然有各种新的研究成果不断证实色彩的存在，但还是有更多人认为这些雕塑本来就是单色、白色或材料原色的。但留传条件、近东文化，埃及雕像和伊特拉斯坎雕塑与古希腊的类似，正是它们留传至今的至多为微不足道的残片或模糊的色彩痕迹，使人依稀感受到古代雕像彩绘曾经的丰富和艺术质量。

在过去 20 年里，中国出土了成千上万的陶俑，有些大如真人，有些身高不过寸许——几乎所有这些雕塑表面都敷彩，其中不少陶俑还保留着它原始的彩绘。毫无疑问，这几十年中最著名的考古发现当属秦始皇陵。不仅兵马俑，而且其它大批人俑、动物俑类的陪葬品也全部彩绘，通过这一切和强烈的色彩，让人领略到之前无人能够感受的活生生的古代雕塑和其感染力。

在这次研讨会中，来自世界各地的学者们有的针对中国出土文物，有的涉及埃及、近代与欧洲的范畴。他们探讨了服饰色彩在不同文化中的象征和意义，还从自然科学和修复工艺的角度，对绘画工艺、颜色材料及保护问题进行了介绍和交流。

论文收集了研讨会上发言人所做的报告。它们勾勒出了古代雕塑彩绘的概貌，探讨了古代文明在雕塑表面表现方法上的异同。从中我们可以看到，仅仅是在蓝色应用方面的相似性令人惊奇，而且在古代雕塑表现方法上也十分类似，可以推测，早在古代，多文明之间的文化交流便已相当密切。

这次研讨会的所有组织者——秦始皇兵马俑博物馆、巴伐利亚州文物保护局和德国国际古迹遗址协会——都怀着这样的愿望，那就是将古代雕塑彩绘的研究和文化交流继续进行下去。

我们对所有发言人所做的报告，对与会者对此专题持有兴趣表示感谢。

我们还想向陈钢林博士先生表示谢意，他作了前言前所有中文报告的准备和编辑。伊赛妮·墨尔姆斯希-舍勒博士女士作了英文校订。

最后要衷心感谢卡塔琳娜·布伦斯多福修复师女士，秦俑博物馆的郭宝发副研究员、赵昆、夏宜等先生，这次研讨会的准备和组织工作，正是他们一道完成的。

张延浩局长
陕西省文物事业管理局

吴永琪馆长
秦始皇兵马俑博物馆

埃贡·约翰内斯·格莱佩尔博士
巴伐利亚州文物保护局局长

米夏埃尔·佩策特博士教授
国际古迹遗址协会主席
Michael Petzet

Introduction

Opening speech held in Xi'an, March 22, 1999

We have come together here in Xian, the old Chinese imperial city, on the occasion of the discovery of the First Chinese Emperor's world-famous terracotta army 25 years ago. Eleven years ago I travelled to the People's Republic of China for the first time together with Dr. Döll from the Federal Ministry of Research and Technology and with Dr. Weidemann, my colleague from the Roman-Germanic Museum in Mainz. On this journey first arrangements for the cooperation with representatives of the Province of Shaanxi were made. I had no idea then how and to what extent these agreements would have an effect on matters of conservation practice. Today, I am especially pleased to see that many of the representatives with whom these arrangements were made are present. I am sure they can remember as well as I do how we started this cooperation together. I am particularly grateful to name, as representatives of many others, Minister Zhang Tinghao and Director Wu.

Ten years ago the People's Republic of China was facing tremendous transformations. Most of all the economic changes of the past decade in China continue and affect the lives of millions of people with breathtaking speed. In Germany, as well, the reunification of both German states has caused many changes. Furthermore, the overall structure of Europe has been transformed. I am not here to talk about international politics. However, conservation practice and archaeology in particular are closely related to politics, to economy and the development of states in general - a relation which is much closer than normally assumed. The new building of the Xian Museum, for example, would not have been possible without the economic upturn in China, and the new airport of Xian is directly linked to the archaeological discoveries in Lintong. The majority of the sensational archaeological discoveries not only in the Province of Shaanxi but everywhere in China, cannot be separated from the terrific economic development. In our modern world conservationists here in the Province Shaanxi are faced with tasks and problems unheard of until then. These problems include the sheer amount of archaeological finds and their exceptional quality, the question of financing, logistic and administrative tasks. And here, apart from the daily tasks which those who work for conservation offices or museums in China have to cope with, the readiness of China to cooperate internationally was, from my point of view, an important prerequisite for managing the problems of preserving the monuments and archaeological sites. As President of ICOMOS Germany I am familiar with conservational challenges in many countries. Therefore, I may emphasise that the results of our joint efforts, some of which discussed in our conference, are extraordinary and deserve international attention.

Our cooperation resulted not only in contacts with the relevant German institutions, but also in contacts with colleagues in Switzerland, France, Italy, Japan and the United States. Conservation practice and archaeology and, in this context, science and research in the widest sense have a common responsibility to protect the historical heritage of mankind, in particular the monuments and sites on UNESCO's list of the world's cultural heritage. One of the most beautiful and impressive monuments of this category is undoubtedly the tomb of the First Chinese Emperor. The unique terracotta army is not merely a gigantic example of the antique burial culture, but, in fact, it is also the largest complex of antique sculptures discovered so far. With this spectacular discovery China has gained an outstanding position in the history of sculpture and is thus equal to the other antique civilisations in Greece, Rome or Egypt. The terracotta army has enabled China to fill people all over the world with enthusiasm about the Chinese civilisation and to redefine the status of Chinese culture. Well-known as the Chinese Wall may be, being the only building that can be seen from space, for the last 25 years Chinese civilisation worldwide has most of all been identified with the terracotta army. For millions of people the chance to see these sculptures in the original remains a lifelong dream. The opportunity for me and my colleagues not just to visit these monuments but to actually take part in their preservation has been one of the most wonderful experiences of my career.

Antique sculptures were polychrome. Not only in China but also in other antique civilisations sculptures were painted in colours. Although this has been known among experts since the 19th century, scholarly work, analysis of the technique and the interpretation of the meaning of polychromy are still at the beginning. Therefore, we are still far away from a comprehensive idea of what antique sculptures originally looked like. The lectures at this congress will focus on such questions as the materials. Considering the fact that these sculptures were in wet soil for over 2000 years the analysis is a challenge even to modern science. All over the world natural science in our days is confronted with unprecedented radical changes. Despite spectacular scientific achievements research on archaeometry has only just started. Advances in natural science need to be made use of for our aims. It gives me great satisfaction to know that for our joint research on the polychromy of the terracotta army we have been able to employ the latest methods and technologies and that on the occasion of this project, the restoration workshops of the Bavarian State Conservation Office have been equipped with these technologies. In the following lectures we will learn a great number of details of these modern methods.

Not only antique sculptures but also antique textiles were coloured. An understanding of the polychromy of antique sculpture is therefore only possible by understanding the types of antique clothing. Knowledge of antique clothing is a prerequisite for the understanding of the painted surfaces of the warriors. Some of the lectures on this topic will try to bring coloured sculpture and textiles together and thus bridge the gap between two isolated fields of research. Knowledge of real textile finds can be supplemented by the "documentation" as found in the colour scheme of antique sculptures - a method that has been used far too rarely. It is high time that classical archaeology pays more attention to the results of textile research. Due to its
silk production the old Chinese Empire again had an outstanding position, whose influence on late antique and early Christian cultures cannot be overestimated. The history of the silk route has not yet been written comprehensively. Recent findings along this trade path offer new clues to the understanding of the cultural exchanges in the Antiquity. The idea that antique China was totally isolated from the other antique empires is completely outdated and is disproved by each new discovery.

As far as I know, it is for the first time that an international congress is held which focuses on the polychromy of antique sculpture in a global context. Usually, research concentrates on regional problems and developments, and only very rarely a scholar who, for instance, is working on aspects of the classical Greek period, can get an overall view of the latest results of contemporaneous civilisations. Xian, starting point of the antique silk route, is also for that reason predestined to hold a conference where relations, connections, interdependences, but also cultural differences in the antique world can be discussed.

The congress "Polychromy of the Terracotta Army of the First Chinese Emperor Qin Shihuangdi", organised by the Museum of Terracotta Warriors and Horses, the Bavarian State Conservation Office and ICOMOS Germany does not, of course, show all the results of a decade of German-Chinese collaboration in the field of conservation practice. This collaboration has been generously supported by the German Federal Ministry of Education, Science, Research and Technology and recently also by the Bavarian State Government. It is therefore my privilege to send you the regards of the Bavarian State Government and in particular of our Minister of Science and Art, Hans Zehetmair. An important result of our cooperation with the Office for the Protection of Cultural Goods in the Province of Shaanxi has been the realisation of a conservation concept to preserve the unique grotto temple of the Great Buddha of Dafosi near Binxian. The results have already been published by our Conservation Office. The results of our collaboration with the Museum in Lintong on questions of preserving the terracotta army will also be published soon.

The opening of our conference is another occasion to thank Minister Zhang Tinghao and all Chinese colleagues, especially Wu Yongqi, the director of the Museum in Lintong, as well as his predecessor, the famous archaeologist Professor Yuan Zhongyi. Moreover, I have to thank all those colleagues from the Bavarian State Conservation Office who have been involved in the China project, particularly Prof. Emmerling and Prof. Stengers.

I am glad that this congress here in Xian has been made possible and I am convinced that it will be a great success. Perhaps it would even be interesting if the topic of our conference could be discussed again in Xian in ten years time, exchanging once again the latest results. Apart from that, a special concern also will be to further develop the friendship that arose in the course of the last years between the Chinese and German colleagues, using our combined efforts to seek ways to preserve our great cultural heritage.

佩策特

序言

1999年3月22日在西安开幕式上的讲话

值世界闻名的秦始皇兵马俑发现25周年之际，我们汇聚到西安这座古老的中国皇城。11年前，我第一次来中华人民共和国旅行，同行的尚有联邦德国研职部的德郎博士和我的同事，古罗马-日尔曼中央博物馆的魏德曼博士。此行为与陕西省的单位合作拉开了序幕。我们签订的协议将如何和在何种程度上，对文物保护方面的合作产生影响，对此我当时尚无明确的概念。今天，当遇见许多当年参加我们会谈的伙伴也在场，欣慰之情，油然而生。我敢肯定，他们同我一样，对我们合作的起步还记忆犹新。在这里，请允许我怀着由衷的谢意，提代表许多的两位的名字，张延皓局长和吴永琪馆长。

十年前，中华人民共和国面临巨大的改革。过去十年里，中国发生的经济变革最为显著。这一变革没有终止，而且正以惊人的速度改变着成千上万人的生活。在德国，两德统一也带来了某些变化，连欧洲的整体结构也变了。我在这里并不想谈论国际政治，但是，文物保护，尤其是考古与政治，经济和国家的整体发展不无联系，其联系比一般人想象的要紧密得多。没有中国的经济发展，譬如就不可能有西安的陕历历史博物馆的新馆，而西安新机场的建成，则与临潼的考古发现息息相关。不仅陕西省，而且在中国各地，大量令人惊异的考古发现均与飞速的经济发展有着不解之缘。当今世界，文物保护工作者在陕西省所面临的任务和问题都是
空前的。问题不仅在于这儿考古发现的数字之众，质量之精，而且涉及经费、后勤和管理。姑且不论中国文物保护工作者和博物馆专家所要对付的日常任务，在我看来，中国愿意进行国际合作，乃是有效解决古迹和考古遗址的保护问题的一个重要前提。因为是国际古迹遗址协会的主席，我熟悉许多国家的文物保护工作。因此，我可强调指出，我们双方共同努力的结果是不完全相同的，应受到国际上的重视。在这次研讨会上，我们将有机会对部分成果进行评论。

我们的合作单位不仅包括有关中国的专业机构，而且还有瑞典、法国、意大利、日本以及美国的同事。文物保护和考古，在这一点上，还有最广义的科学和研究，都要共同对保护人类的历史遗产，尤其是联合国教科文组织名单上的世界文化遗产负责。不言而喻，这一级别中最美、给人印象至深的文物之一，就是秦始皇帝陵。举世无双的兵马俑不仅是古代墓葬文化的巨制，而且事实上也是迄今为止所发现的古代陵墓中最大的群体。由于这一引人入胜的目的，中国在世界陵墓史中也获得了显著地位。可与古希腊、罗马和埃及文明相媲美。通过兵马俑，中国能唤起世人对于中国文明的热情，中国文明的地位因此也要重新定义。尽管中国长城闻名遐迩，她还是中国文明的唯一建筑。但在中国25年里，世界上大多数人均把兵马俑与中国文明作等量齐观。亲眼目睹真实的兵马俑，对成千上万的人来说，是毕生的愿望。至于我和我的同事不仅有机会参观这些文物，而且竟然能亲身参与保护它们，这不能不说是我国事业中最美妙的经历之一。

古代雕塑是教科书的，不单在中国，而且在其它古文明中的雕塑也经过彩绘的。即使这一事实自19世纪以来已为专家所了解，但科学研究、技术分析乃至对彩绘工艺的阐释仍然处于起步阶段。因此，古代雕塑的外观究竟如何，我们的认识还是非常不全面的。这次研讨会上，将有报告专门探讨诸如有关彩绘材料方面的问题，鉴于这些雕塑在湿土下埋藏了2000多年，即使对现代科学而言，分析工作也并非不是一种挑战。当今世界各地，自然科学家面前严峻的转变。尽管这些科学成就引起轰动，可是考古学的史研究才刚刚开始。为了我们的目标，我们要充分利用自然科学的进步。我感到十分欣慰的是，在共同研究兵马俑的彩绘时，我们成功地使用了最新的方法和工艺，项目着手之际，巴尔利亚州文物保护局的修复车间已掌握了这一工艺。在下面的报告中，我们将会更多地了解这些先进方法的细节。不仅古代雕塑，而且古代纺织品也都上过彩。因此，只有理解古代服饰的形式，才能理解古代雕塑的彩绘。对古代服装的认识又是了解兵马俑表面彩绘的前提之一。这次会上的有些报告将围绕这个专题，在彩绘雕塑和彩绘纺织品的综合观察上进行尝试，从而消除两个孤立的研究领域之间的隔阂。对出土纺织品的认识可以作为补充文献，来说明古代雕塑的彩绘配色，然而难以有人使用这种方法。古典考古学应立即更加重视纺织品的研究成果才是。古代中国因以丝绸生产而占优先地位，她对古代晚期和早期基督教文化的影响及评价并不会过高。全面的丝绸之路史尚未有人撰写。这条贸易之路迄今仍在使用，沿路最近的考古发现将会对世界古代文化交流提供新的线索。将古代中国与其它古代帝国彻底隔绝的观点已完全过时，这一点在每次考古新发现中都得到了证实。

据我所知，举办以世界范围的古代雕塑彩绘为题的国际研讨会，这是第一次。通常情况下，研究集中在地区问题和发展上，一个以从事研究希腊古典时期的学者，又能通观同时期其他文明的最新成果，实在是凤毛麟角。西安是古代丝绸之路的起源，也是基于此因，注定要在今年举行研讨会，来探讨古代世界不同文化的关系，交往，相互依存以及彼此差别。

这次"秦始皇帝兵马俑彩绘"研讨会会由兵马俑博物馆、巴尔利亚州文物保护局和德国古迹遗址协会共同举办，当然不能展示这十年间，中两国在文物保护领域合作的所有成果。这一合作得到了德国政府、科学研究所的经济援助。最近又得到巴尔利亚州政府的赞助。因此我很荣幸向你们转达巴尔利亚州政府、尤其是我们的科学和艺术部长的汉斯·施密特迈尔部长的问候。我们和陕西省文物保护局合作的一项重要成果，是实施保护独特的秦始皇帝陵的维修方案。该成果已由我国国际合作局出版，我们与临潼秦俑馆合作保护兵马俑的成果，也将会不久公布。

研讨会开幕之际，我想向张延皓局长和所有的中方同事表示祝贺。特别是临潼秦俑馆的吴永琪馆长及他的前任、著名的考古学家袁庆厚教授致以谢意。此外，我还想向参加中国项目的巴尔利亚州文物保护局的所有同事，尤其是艾默林教授和史奈特拉教授表示感谢。

这次研讨会能在西安举行，我很高兴，我相信，她一定会取得圆满成功。如果十年后，又在西安讨论研讨会的专题，重新交换新成果，那将是饶有兴趣的。此外，我们特别关切的是，继续发展多年来在中、法双方同事间建立的友谊，经过我们共同的努力，去探索保护我们伟大的历史遗产之途径。
秦始皇帝兵马俑服装的颜色

秦兵马俑坑是中国历史上第一个封建皇帝秦始皇陵园中的重要陪葬坑，距今已有2200多年的光辉。兵马俑坑内陶俑、陶马约8000余件，其中以车、骑、步兵等不同的兵种。它是秦始皇所修筑的军队作为原形塑造的，是秦军的缩影。陶俑身上原来涂绘彩绘，每处出土的陶俑颜色大部已脱落，仅存微量的残迹。个别的残存的颜色较多，色彩如新。通过陶俑身上残存的色彩，可以大体上了解两千年多年前秦人对服装的爱好和审美情趣等许多社会问题。

一、陶俑彩绘颜色的出土情况

兵马俑出土的陶俑身上残存的彩绘颜色，主要有红、绿、蓝、紫、黄、黑、白等，各色在色调上因深浅浓淡的不同而有多种不同的色阶。

陶俑身上原为全彩绘，但在俑坑建成初期因山洪爆发陶俑被水浸泡，公元前207年又因农民起义等火烧了俑坑，经过这两次大的劫难，陶俑上的彩绘颜色已大部分脱落。陶俑出土时仍存有的颜色，一部分已和陶俑脱离粘附在泥土上，有些颜色虽仍存留在陶俑身上，因埋在地下两千多年受自然的破坏，颜色对陶俑的附着力已很脆弱极易脱落。

彩绘的方法：是先将一层生漆作底，在底层上再涂绘彩色颜料，层厚约0.03-0.06毫米，颜色层厚度为0.01-0.04毫米。生漆作为底层的作用是使彩绘的表面涂蜡粘合，吸水适度，利于施色，并增强颜料的附着力。在陶制品上彩绘以生漆作底的技法创始于秦，流行于汉，汉以后除旧，似乎已被使用胶水涂水来绘画材料的方法所取代。

颜料的物质成分经分析鉴定：大都是天然的矿物颜料，其中的紫色、绿色和红色被认为是用化学方法制造的。紫色为硅酸铜，这种物质是古代八十年代才被偶然发现而为人们所认识的。在自然界中未见发现。关于暗红（2PbCO₃，2Pb(OH)₃）和淡绿（PbO）的制造，分别见于公元前4世纪的《吕氏春秋》和公元前2世纪的《淮南子》等两书中。兵马俑彩绘颜料中的硅酸铜是和红色和绿色的发现，进一步证实了中国古国在两千多年前已能采用化学方法制造颜料，在科技史上具有重要的意义。

二、各类不同陶俑的服饰颜色

一、二、三号兵马俑出土的陶俑，以其身份地位的不同可分为军俑俑和一般士兵俑两大类。而军俑俑中又有高级军俑俑和中级、下级军俑俑的区别。一般士兵俑中又有车兵、骑兵、步兵等不同的类别。这些不同的武士俑佩带颜色的情
从上面列举的各自不同身份，不同兵种的陶俑身上的服装颜色，可以获得如下两点新认识：

第一，秦国的军队除铠甲之外没有统一的服装颜色，上衣和下衣的颜色都是多种多样，而各军所好，不拘一格。不但车兵、骑兵和步兵三大兵种服装的颜色不统一，而且每个兵种内部也没有统一颜色的服装，就连同一辆战车上的三个乘员的服色也大相径庭。这说明秦国没有统一的军服。

秦国实行的是征兵制，农民是被编入国家户籍之内，接受一定的军事训练，战时被征入伍，战争结束即回家种田，服役的年龄为17-60岁。服役期间除铠甲和兵器外由国家配给，身上所穿的衣服都是自备的。湖北省云梦县睡虎地四号秦墓出土的衣物的上衣有木俑上的家信，是参加攻秦的军士在函谷关与弟二人向家中写的要衣服和钱的家信。内容为：木俑(M4:11)黑衣的家信：“黑衣，母夏衣来。今书”(到)事，母亲安乐寡居，可以为衣被着，母必为之，今与藤衣来，其藤衣厚，得以衣，黑衣自布此。黑衣等作众行军，攻反城之，速能可智，也，愿诵黑衣用勿少……”木俑(M4:6)的家信：“……愿母速来……”百六，布建事者毋二丈五尺。……”(用简牍文字，其字)“侍，即死也。急急急。”这两封信清楚地说明秦军的服装是自备的，军中的零花钱也应从家中索求，秦人从军纯是尽义务，没有俸禄，兵马俑武士俑的服装和服色，实际是当时秦国军籍上流行服色，服色，是秦人服饰文化的真实写照。

第二，秦国军队中服色的服装颜色没有等级的区别，也就是说军装和一般士兵，以及军官中的高级军官和中、下级军官，彼此之间所穿服色的颜色，都没有明显的区别，而是各自随所好。秦军反映等级高低主要标志在冠与铠甲的颜色，高级军官，头戴冠，穿彩色鱼鳞甲；中低级军官，头戴单色长冠，穿带彩色边花的铠甲；下级军士，头戴单色长冠，不带彩色花纹的铠甲；一般士兵，头上一律不戴冠，穿的甲衣皮片比较甲，上不带彩色花纹，上不带彩色花纹的，上述情况为以后人们所不知，为考史书上首次发现，它不见于文献记载，可补史书之缺。

三，从陶俑身上的衣服看秦代服饰的流行色

根据兵马俑坑出土的各武库俑身上残存的服色，大体可以了解秦人对服装服色的爱好于感情。

上衣的颜色：已出土的武士俑身上的衣服有颜色残迹，明确其上衣的颜色者，计277件俑，其中穿红色上衣者88件，粉红色118件，粉色52件，天蓝色16件，白色2件，褐色1件，可见绿、红、紫三色是上衣的主色，分别占总数的42.6%、31.8%、18.8%。天蓝、白、褐三色数量很少，分别占6.7%、0.4%。上衣的色彩以红色、粉红色、天蓝色为主。

下衣的颜色：下衣即长裤和短裤，根据俑身上存留的颜色残迹，可知下衣的服色者计425件俑，其中穿绿色下衣者232件，红色78件，天蓝色61件，粉色50件，白色13件。这说明下衣的主色为粉红色，占总数的52.5%，其次为红色，天蓝，粉紫三色，分别占18.4%、14.4%、11.8%。白色为少数，占3.1%。

护腿的颜色：护腿分为两种，一是圆筒形的一节护腿，二是护腿分为上、下连成的两节，节色不同，现以第一种护腿为例说明其服色。根据颜色残迹可明确其服色者计177件俑，其中穿粉绿色护腿者102件，白色7件，可见护腿是用绿色为主色，占总数的57.6%，其次为粉、紫、红、天蓝，分别占16.4%、11.3%、10.7%、白色最少，占4%。

头领的颜色：根据182件陶俑领上残存的头领颜色遗迹，其中绿色领68件，粉绿色50件，未注明颜色26件，白色18件，天蓝色10件。可见以绿色和粉绿色数量最多，分别占总数的37.4%、33%；其次为未注明颜色，占14.3%；白色和天蓝色数量较少，分别占9.9%、5.5%。

袖领的颜色：袖口的颜色有单色和双色两种，此里仅以单色袖领为例，单色袖领目前发现239件，其中绿色99件，粉绿色80件，未注明颜色47件，天蓝色8件，白色6件，可见以绿色、粉绿色数量最多，分别占总数的41.4%、33%；其次为未注明颜色，占19.7%；天蓝色、白色分别占3.3%、2.1%。

从上面的统计数字，我们大体可以了解两千多年前秦人最喜欢的衣服服色是什么。上衣，最喜欢的是绿、红、紫三种颜色，其次是天蓝色，个别的为白色、褐色。下衣，秦人最喜欢的是绿色，其次是红、天蓝，粉紫三种颜色，个别的为白色，护腿，秦人最喜欢的是绿色，其次是粉红、红、天蓝三种，这说明当时秦人的服装以绿、红、紫、蓝、白为流行色，其中尤偏爱于绿色。另外，在上衣的领部和袖部都镶有彩色的花边，使之绚丽美观。

对上衣和下衣以及衣服上镶的花边的颜色，秦人非常讲究服色的搭配，喜欢强烈的对比色，绿色的上衣，一般着粉紫色或红色的衣服，下身穿天蓝色或枣红色的裤，红色的上衣，其领和袖口一般是着绿色或粉绿，天蓝色的衣服，下身穿深绿或粉绿色裤，这种上下衣服用强烈的对比色，色调鲜明，服色绚丽。秦人的服色给人的感觉，感情和精神力量是热烈、喜悦、活泼、热而又深沉。秦人这种审美的情趣，反映了其积极的生活内容及蓬勃向上的正面审美价值。

服色的代表者是一个国家、一个民族的审美观和思想感情，服色的服装又是随着时代的变化和生活习俗的变化而不断发展变化的。而同一时、同一民族又有时尚色和民间流行色的区别。中国历代的时尚色，传说的黄帝时代尚黄，夏代尚青，商代尚白，周代尚红，秦代尚黑，汉代及其后各代均尚黄，时色尚是当时最尊贵的颜色，绝不是说全国人们都穿一种颜色的衣服。秦始皇统一全国采用了黑色作为最尊贵的颜色，有重大的典礼活动皇帝要穿黑色的服装。从兵马俑坑出土的武士俑的服色颜色，可以说说明民间流行的服装颜色与时尚色很不相同，民间喜爱的是颜色鲜艳的服色。时色尚多含有政治或道德、伦理、传统性习惯等方面的因素，而流行色则是反映人们审美情趣的艺术潮流趋向的单纯色彩倾向的表现。所以兵马俑的服色反映了当时人们审美艺术潮流的趋向。

在阶级社会里，什么阶层的人穿什么颜色的衣服是有严格规定的，一般庶民只能穿白色、青色的衣服。而秦王朝时期却打破了这个限制。这是因为自春秋战国之际开始，随着
The Costume Colours of Qin Terracotta Warriors

Yuan Zhongyi

The originally coloured warriors bear different colours of red, green, blue, yellow, black, white, etc., each with various tints. The application method of the diverse colours is as follows: the first coating serving as the background followed by different colours for the diverse pieces of clothing. Characteristics of the costume colours of Qin warriors are:

1. Their costumes are brightly coloured with green, red, violet and blue as the chief colours and white and black as auxiliary tints. The clothing for the upper and lower body are in sharp contrast with coloured laces. The colours are warm and bright. In the Qin Dynasty, there was no uniform for the soldiers. They were expected to prepare their own clothes, hence the variation of colours. People at the time were interested in bright colours.

2. There was no remarkable difference between officers and simple soldiers in the colour of their dress. Nor was there a strict distinction between generals and inter-mediate and low-ranking officers. Everyone was free to choose his dress colour out of red, green, blue, violet, etc. It is a reflection of the free atmosphere of the Qin people at a time when the hierarchy of the old slavery had been broken and the new feudal system had not yet been established.

3. Even for the three ranks of the Qin army: chariot soldiers, mounted soldiers and foot soldiers, there was no unified costume colour. The cavalrmen were beginning to wear slightly different clothes than the chariot and foot soldiers (Hu clothes), but there was no distinction in colour.

4. Warriors from the pits wore different armours in different colours if they were of different ranks. Only the high-ranking officers like generals and the intermediate-ranking officers wore armour with exquisite patterns whereas the low-ranking officers and common soldiers wore black armours.

The Qin Dynasty used a conscription system under which armours and weapons were issued by the government while clothes were prepared by the soldiers themselves. Most of the soldiers were farmers. The forms and colours of the warrior's costumes reflect the taste and life style of the time.
Aims and Results of the Chinese-German Project for the Preservation of the Terracotta Army

"How the Ancients Portrayed Death" is the title of a famous work of literature written by the German poet Gotthold Ephraim Lessing in 1769. In this essay, Lessing gives a detailed description of the "Ancients" (the Greeks and Romans) depicting death not as a macabre skeleton but instead personifying it as a winged genius. The horrible and drastic depiction of the skeleton as a "dead man" is a post-Antique conception, influenced by Christianity and especially prevalent in the Middle Ages. At this congress, I hope to learn more about how the ancient Chinese conceptualised death.

Despite its massiveness and huge dimensions, the terracotta army was "only" a burial furnishing which until now has often been misunderstood. For many years now, Professor Yuan has done research on the discovery as well as on the function of the terracotta army of the First Emperor. Furthermore, he has also published the existing descriptions concerning the content as well as the arrangement of the actual burial chamber or tumulus grave. How death was conceptualised is still not known. We merely know about the burial rites, rituals and fashions. Since we are dealing with "colour" in our joint project, it would of course be very interesting to learn more about the colour of "death" in China.

In burial sites found in Germany from the same period no known life-size sculptures have been discovered. Similarities may be found in the grave goods such as weapons, vessels, textiles and bronze objects required for daily use.

The antique sculptures in Germany are almost exclusively an inheritance from the Roman Empire. Nevertheless, a joint project between the Terracotta Museum and the Bavarian State Conservation Office concerning the conservation of the polychrome terracotta soldiers has been realised. The state restoration workshops of Bavaria have intensively studied the conservation of sculpture polychromy of the last 100 years. Conservation work has been done on countless wooden and stone sculptures dating from 1000 AD and later in the state restoration workshops.

In comparison with medieval sculptures, the restoration of polychrome surfaces of antique sculptures is a topic that has only been dealt with on the surface. For the majority of sculptures from Greek and Roman civilisations as well as Near East civilisations, research on polychromy has until now remained an unfulfilled desire. This is due to the fact that polychrome surfaces from these civilisations have rarely survived, were lost during excavation, or were removed shortly thereafter to show the "pure form" of the sculpture. Even though the polychromy of the terracotta army is in a very fragmented state, the impressive artistic quality has been preserved on countless fragments. For the first time in the history of archaeology, one of the main goals of an excavation is to also preserve the polychromy, which has been partially possible due to the exemplary excavation. Archaeologists in China have taken the opportunity and responsibility and have avoided the errors that were committed during excavations of Mediterranean civilisations in Europe. The practice of erecting huge protective structures over excavation sites, so that all archaeological treasures can be left where they were found in their own excavation museums is firmly established in China (e.g. with Neolithic objects in Bangou). The opportunities and possibilities of this type of preservation of the stratigraphy of the excavation and presentation of the findings can be observed in the very difficult situation in Pompeii, where great efforts will have to be made to save the original situation there before it deteriorates further.

Countless conversations during preparation for this congress confirmed that, at present, research concerning the polychromy of antique sculptures does not receive a great deal of academic attention. Summaries on this complex topic concerning iconography, knowledge of materials, restoration and scientific aspects do not exist. Even today "colour" used for the design of antique sculptures is still a "blank" on the map of archaeology. This lack of attention might almost give the false impression that we are grateful to earlier generations of archaeologists and restorers who, in their work, attempted to eliminate the problem of preserving the polychromy on sculptures by removing every last bit of paint with great effort. Upon discussing the future of the terracotta army, one encounters astonishment when one explains that these thousands of life-size sculptures originally bore a colourful polychromy.

In the following presentations at this congress, the composition of pigments and binding material of the terracotta army as well as possible ways of preserving the polychromy will be discussed. In retrospect, our joint research is not only a success story but also a story of mistakes and failures. If one considers that the chemical composition of a fresh Chinese Chi-lacquer is complex, then one can imagine how difficult it would be to analyse a 2000 year old sample that has been preserved, "stored", under very poor conditions. Today only a few research institutes in the world are capable of analysing such aged material.

For those readers who are not chemists it might be helpful to know that, at the beginning of this century, an artificially produced product called "bakelite" showed certain chemical similarities to "Chi-lacquer". In the 19th century, "Chi-lacquer" could be found in every professional chemical laboratory. It was completely resistant to most chemicals and an extremely durable surface on laboratory tables. Under good conditions, dry atmosphere and no damp ground contact, lacquer particles composed of this material will last thousands of years. Numerous findings in China dating from the Neolithic period and later, prove the amazing ageing qualities of this material. Even more durable is natural resin amber which was originally an organic material whose contents are important, allowing us to reconstruct the ancient DNA structures of organisms trapped in the amber. This
represents an ideal data bank. The resilience that these natural resins have shown over thousands of years is amazing.

The use of Chi-lacquer in China is a very old tradition. Cultivating the lacquer tree plantations as well as obtaining the resin has been a tradition since primitive times. Accounts record that the Second Chinese Emperor wanted his City Wall to be painted with lacquer. But, even considering Chinese standards, this idea, which had a streak of megalomania was not carried out. Similar to silk production lacquer production and craftsmanship is one of the oldest Chinese techniques. It has fascinated Europeans since Antiquity. One only has to recall the enthusiasm for Chinese culture in the 17th and 18th centuries in Europe. The European lacquer technique of the “New Age” is the result of an unsuccessful attempt to imitate the Chinese prototype.

The work we have done together over the years in Lintong and Munich has often focused on very small corroded lacquer particles. The despair we experienced with this very obstinate material often threatened our enthusiasm for the project. Most relevant and even some questionable techniques were tested in order to conserve the lacquer-ground of the terracotta-soldiers. In most cases these attempts failed or had minimal success. The analysis and determination of the pigments of the polychromy was relatively easy in comparison to the treatment of the lacquer-ground, which led to a number of negative results. The identification of the so-called “Han-Purple”, previously an almost unknown pigment, was one of the small highlights of our analysis. Progress over the years was only made by disqualification. May I say a few words to my European colleagues concerning the pigments used, especially cinnabar, a main component of the flesh colours of the terracotta sculptures.

As is well-known, cinnabar is won as a mineral in large deposits which are also found in China. It has served since Antiquity as a pigment, especially for the colour red in lacquerware. At the same time, cinnabar is also an important material in Chinese alchemy and is probably the oldest man-made “chemical” product. Even though the First Emperor was not the first to show a special interest in this material, he encouraged studies on and production of this “magic elixir”. He also strove to obtain more knowledge on the reproducible and reversible reactions of elements such as sulphur and mercury, which generated a great variety of black, red or “silver” coloured effects. Cinnabar, a product of protochemistry, has been known in ancient China since primitive times. Compared to European products the Chinese product is far superior in quality because of the use of very old preparation techniques with natural cinnabar. Even today, it is still extremely difficult to determine which cinnabar (natural or man-made) was the original product. Mercury, a component of this “elixir”, was found in extremely high quantities in the burial chamber of the grave site. As a result of this finding, traditions and rites from the so-called “Seas and Oceans” of the Antique World, which describe the mortuary world of the Emperor in the tumulus, become credible. If the tumulus of the grave should ever be opened, it is very difficult to imagine how one would be able to preserve the volatile substance, mercury.

Considering the sound knowledge of the participating conservators regarding painting techniques, this project would still have been inconceivable without the crucial and decisive information from the participating scientists. I do not know of any other exemplary restoration where the cooperation between chemists, mineralogists and physicists together with conservators and archaeologists has been so extensive. In addition, I know of no other project where all of the different disciplines involved were so interdependent. For most experts, the cooperation of those dealing with the material Chi-lacquer was a new experience that had to be learned. This included not only the restoration studies and institutes in Germany but also the cooperation on an international level.

Last, but not least, the experience and knowledge gained from this joint venture shows that “archaeology”, as a field in conservation, should be perceived in a new light. Furthermore, the status of natural science in conservation should be re-evaluated. It should be taken even more seriously than to date, because we can only adequately treat and protect monuments with the aid of natural science methods. With the conservation work on the terracottaramye the sciences successfully interacted as equal partners. I know of only few projects which have taken place in the restoration studies of the Bavarian State Conservation Office that have been based on such intensive cooperation. Our work with Japanese colleagues on the research project on Baroque and Rococo lacquer techniques should be mentioned here in addition to certain aspects of the conservation of bronze objects.

Cinnabar and lacquers are materials that the conservator is relatively familiar with even though in Europe the raw materials come from different sources. The common link for this congress lies in Arabian traditions, where the origin of modern western chemistry has its roots. Indeed, it is most likely that the origin of Arabian traditions can be traced back to the first contact Arabian scholars had with Chinese traditions. Such cross-references concerning the exchange of knowledge and culture make Chinese Antiquity, as a topic, particularly interesting. It even gives a non-sinologist a notion of the complex structure of ideas in ancient China. The notion of “colour”, pigments, dyestuffs and their production process as conduits for the exchange of knowledge in Antiquity is not new. Recent research emphasising and expanding upon this topic will be presented at a later time by Mr. Berke. Similar conclusions can be drawn in even greater dimensions concerning dyestuffs which were necessary to colour textiles. The parallelism of these developments and the application of these dyestuffs is quite amazing. They suggest that the ancient trading routes transported far more than just pure goods and merchandise.

“Colour” and “polychromy”, used as keys for a deeper understanding and interpretation of antique civilisations, have not been important topics. This congress offers the chance to better understand “colour” and its symbolic function.

Ovid describes amber as “Tears of the Gods” in his collection of myths called “Metamorphosis”. In one of the myths, the daughter of the Sun-God mourns the loss of her brother Phaëthon by shedding “amber tears”. To process raw amber for lacquer, it first has to be melted in heated oil in order to apply it. This was discovered around 1000 AD in the western world. The use of Chi-lacquer as a protective coating on metal to hamper corrosion has been a tradition in China for the last 4000 years. Shortly after the birth of Christ, monumental statues were made consisting of countless layers of lacquer on a support containing hemp. The clay core used in manufacturing was removed after the lacquer had dried and hardened. Considering all that we know about this topic, the use of lacquer as a ground for clay sculptures with a polychromy is very unusual and probably unique to the terracotta army. The lacquer, as material, first became an uncommon and unusual conservation problem due to a combination of a pigmented layer (polychromy) bound by an aqueous binding medium. This binding medium, used together
中德保护兵马俑项目的经验与成果

“古人如何表现死”，系德国作家戈特霍尔德·埃弗拉伊姆·莱辛于1769年发表的一篇著名文章的标题。莱辛在文中详细地描述了“古人”，即古希腊和古罗马人并不是把死表现在死者头骨的骷髅，而是表现在利用头发或装饰的守护神。拿一具赤裸裸的骨架作为死的化身，乃是与古代希腊和中世纪受基督教影响的观念一脉相承的。至于中国的“古人”如何反映死，西方对此所知甚微。

兵马俑的规模虽然庞大，但它们“只是”陪葬品，呈现祭祀礼仪，这一点，西方人常常没有真正地意识到。中国皇帝陵墓中如何以及是否塑造和表现了死，人们还不清楚，我们所知的只是葬礼形式和葬礼。

修复古代雕塑的表面彩绘，是一个有待深入的领域。对大多数古希腊、古罗马包括近东的古代雕塑的彩绘，颇乏研究。主要原因在于保存下来的彩绘表面极其罕见。这些彩绘常常是有意去掉的，以求展现雕塑的“真面”和“新面”。无数的兵马俑残片上残留着原始彩绘，艺术质量突出，能保护和妥善保存秦始皇兵马俑的彩绘，把它作为发掘的纲领性目标来实行。这在考古史上尚属首次。中国考古界为此获得了很多机遇也是任务，避免重犯西方地中海沿岸国家在发掘古代高度文明时所经历的过失和疏忽，从而为抢救出土文物作出榜样。

“中国”和“色彩”依旧有古代雕塑的一个“空白点”，对于颜料和粘合剂的组成成分，我们认识得十分有限。兵马俑身上涂有化学结构相当复杂的漆，由于地下埋置条件不利，2000年后难以查明这种材料有多久。在中国，秦的使用具有悠久的历史，传统漆器的制作和使用在秦汉时期有流传。据记载，秦代5000年左右的漆器，具有5000年左右的悠久历史。至少从东汉初年始，中国已用纸与漆层层相叠，制成高大的夹纻漆器。制作时需要微量，须漆层干后脱模，据我们所知，用漆作为彩绘陶俑的材料，属罕见。这有材料是在与彩绘的陶器粘合的颜料结合时，才成为保护的难题。我们未能找到彩绘颜料的粘合剂，也许该材料已被彻底分解了。

在我们研究的头几年，我们倾向于用这种材料结合的废料进行研究。经过对这个问题的探索，很遗憾，我们对中国古代工艺依旧认识不全，但是我们今天判断更谨慎了，这一失误，与其说是在古代的绘画工艺中，倒不如说是应在我所残缺的认识中去找寻。
秦始皇兵马俑彩绘保护研究回顾

秦始皇兵马俑彩绘保护研究，是随俑坑的发掘而开始的，至今已近25年了。现将彩绘保护国际研讨会召开之时，对秦兵马俑彩绘保护研究予以回顾，以便有助于文博工作者对其保护研究状况的了解。

秦始皇兵马俑三个坑内埋藏着真人真马般大小的兵马俑近8000件，这些兵马俑原来都通体涂有彩绘。由于俑坑在塌陷之前，曾遭受火灾和洪水的浸泡，以及塌陷以后，兵马俑埋于潮湿的填土之中，受到地下有害介质的长期侵蚀，因而彩绘受到了很大的损坏。出土时，附着在兵马俑体上的颜色残迹，也由于上述原因，已变得非常脆弱，暴露于自然空气环境下很快发生起翘、剥落(彩图1.1)。

为了妥善保护这些珍贵的彩绘残迹，在一号坑前五探方发掘期间，单克、韩汝芬、李亚东等人就彩绘的物质成分分别进行了测试分析，单克老师还对彩绘的加固保护进行了实验研究，并处理了一些俑头上残存的彩绘。在二号俑坑发掘期间，我和周铁对彩绘剥落原因进行了试验研究，采用研究出的综合保护工艺处理了一些俑上的彩绘残迹。1992年，陕西省文物局和巴伐利亚文物保护局开展了合作研究秦兵马俑彩绘保护的项目。中方人员先后有4次。9人次。累计16个月在巴伐利亚州文物保护局，与德方同事共同就兵马俑彩绘保护问题进行系统研究。下面各阶段的保护研究情况予以回顾。

1. 一号坑前五探方发掘期间彩绘的保护和研究

这期间(1974年-1982年)所做的工作，根据已发表的文献资料来看，有两个方面：一是对彩绘材料的调查；二是对彩绘加固的探索。在彩绘材料分析方面，除了紫色和黄色颜料层以及黄褐色物未查外，其它颜色层物质皆已查明。在彩绘加固方面，最先采用加大分子量的聚丙烯酸酯(以下简称PEG)水溶液进行加固，效果欠佳，后来改用水溶性聚丙烯酸酯类等加固剂进行加固处理。保留了一些俑头上的残存彩绘。综合来看，这时期所做的工作还不够系统全面，尤其在彩绘的加固保护上，做的试验研究还不够充分，属于秦兵马俑彩绘保护研究的初期探索阶段。

2. 三号俑坑发掘期间彩绘的研究和保护

在三号俑坑发掘期间(1988年9月至1989年9月)，起初采用聚丙烯酸酯乳液对出土后的彩绘进行加固处理，但发现处理过的彩绘，在自然环境下，还会发生剥落。为了查明彩绘剥落的原因，对经过加固和未经过加固的一些彩绘残片进行了跟踪调查，结果发现；环境湿度变化，引起彩绘脱落失水，与彩绘剥落有密切关系。为此针对这一点，将一些未经处理的彩绘陶片分别放置于一系列相对湿度不同的恒温器内进行干燥实验。结果表明：恒温器内的相对湿度越低，彩绘剥落得越快；在恒温器内湿度高于93%R.H.的条件下，彩绘较长期附着于陶器上而不发生剥落。另外，调查发现，凡对环境湿度有影响的自然和人为因素都会加速彩绘的剥落。这时期，为了配合俑坑的展出，还探索出了潮湿状态下的彩绘修复工艺。基于彩绘剥落原因的调查结果，结合潮湿状态下的彩绘修复工艺，提出了一套秦俑彩绘的综合保护措施。主要包括使用丙烯酸加固、环境湿度下完成修复、稳定环境下干燥等，并对一些俑上的彩绘残迹进行了保护处理，取得了一定的成绩。但这阶段的工作，总的来看，还显得较粗糙，缺乏对彩绘保护问题的系统研究，也未能从根本上解决兵马俑彩绘的保护问题。

3. 中德合作以来彩绘的保护研究

自1992年中德合作以来，对兵马俑彩绘保护问题进行了全面深入的研究，取得了丰硕的成果：

3.1 对彩绘构成和施彩工艺的研究

3.1.1 彩绘构成

对彩绘构成的调查主要是通过显微镜技术进行的。调查结果表明：秦兵马俑彩绘在层次结构上很不统一。有的由一层生漆层和一层颜料层构成。这种结构类型的彩绘在秦俑彩绘中占绝大多数。并出现在除褐色以外的各种颜色层当中的。有的由两层生漆层和一层颜料层组成，该类型主要出现在一些俑袍底的红色涂层中。有些由一层生漆层和两层不同颜色的颜料层构成。这种类型主要涂在一些俑的脸上，手或身体；个别俑的局部涂层是由生漆底层和双颜料层组成的；也有的彩绘仅由一或两层生漆层构成。这种纯生漆涂层主要出现在甲俑的铠甲上以及某些俑的发髻和足履上。单层生漆层厚约0.03毫米；粉红色颜料层最厚，0.09-0.20毫米；红色颜料层最厚，0.01-0.04毫米。

3.1.2 施彩工艺

关于施彩工艺的调查是基于发现在场的实际观察和对一些彩绘残片的显微调查得出的。调查结果表明：兵马俑彩绘是用涂刷法实施的(彩图1.2)。彩绘工艺过程是：第一步，用腻子对陶器表面进行抹光处理(彩图1.3)。这一处理步骤具有针对性，并不是所有兵马俑都经过这一处理步骤。所有兵马俑在制作泥胎时，表面都经过抹光，压光处理，出窑后
绝大多数兵马俑表面细腻光滑，彩绘时就直接在陶表面进行，而对表面凹凸不平的，才用这一处理步骤。第二步，在陶胎或胎表面涂刷1-2层生漆。第三步，配好与对象要求色调基本相符的颜料，用稀释水调和均匀，涂刷于生漆底层之上。有些部位，如表现皮肤和指甲盖等部位，一些涂饰了不同颜色的颜料层。第四步，对细部进行涂刷或晕染，例如，眉毛、胡须等。

3.2.2 颜料物质成分分析

3.2.2.1 颜料物质成分分析

关于颜料的物质成分，在中德合作项目中，进行了许多分析。曾进行了一些分析、推测。结论一：有人经过分析，判定为金银合金等。认为的彩绘是用明胶打底；有人根据我国的绘画传统，认为其是我国古代特有的、施用于生漆底的技法；也有人提出过生漆材料，但缺乏科学检测依据。

中德合作项目开始以后，对底层的物质成分进行了多种科学分析。起初，将底层的颜料的图谱和现代颜料层以及可能用到的动物胶的图谱进行比较，发现底层与现代颜料层的红色图谱非常相似。然而，由于底层在地下埋藏了两千余年，已经老化，老化过程的氧化作用会引发变色，而红色图谱在变色过程中会发生变化。鉴于这个原因，对底层又进行了一种处理颜料的图谱，将其进行科学分析。对于底层又进行了更加细致的对比分析研究。

选定的参考样品是与底层的时间相近、老化程度相当、具有明显出土时间和地点的徐州汉代王墓出土的漆棺上的颜料。分析结果显示：其红外谱图几乎没有完全一致，热解气相色谱也显示出高度的相似性。结合底层的假定表示出的极限抵抗能力以及底层与现代颜料层的相似性，从而证明底层是用生漆材料制作。

同时，还对生漆和胶及其它特性，以及生漆使用的资源做了文献研究。认为用生漆涂饰兵马俑是完全可能的。

3.2.2.2 颜料层物质成分分析

颜料物质成分分析主要是采用X射线粉末衍射法和发射光谱分析法进行的。经过多次分析已明确了彩绘颜料的成分，归纳如表1。

<table>
<thead>
<tr>
<th>颜色</th>
<th>成分</th>
<th>说明</th>
</tr>
</thead>
<tbody>
<tr>
<td>粉红</td>
<td>磷灰石+朱砂+铜粉+朱砂或礞石+铜粉</td>
<td>成分不完全确定。</td>
</tr>
<tr>
<td>红色</td>
<td>朱砂+铜粉</td>
<td>成分不完全确定。</td>
</tr>
<tr>
<td>黄色</td>
<td>硫黄+磷灰石</td>
<td>成分不完全确定。</td>
</tr>
<tr>
<td>白色</td>
<td>磷灰石+铜粉</td>
<td>成分不完全确定。</td>
</tr>
<tr>
<td>黑色</td>
<td>炭黑</td>
<td>成分不完全确定。</td>
</tr>
</tbody>
</table>

表1 彩绘颜料成分

从表1中可以看出，除去釉色和铜粉颜料外，其它颜料在我国古代绘画中普通使用，并出现也较早。其中朱砂和铜粉被认为是用化学方法制造的，其它颜料都是天然矿物颜料。

3.3 颜料调和剂的分析

对于秦始彩绘颜料调和时，可能使用何种调和剂，采用了微量元素分析法对其进行试验研究。由于古代使用的颜料调和剂都是溶于水的有机质材料，并长期处于淤泥的泥层下，受地下水等因素的长期侵蚀和传输，调和剂已经分解并严重流失，加之受生漆底的影向及分析方法的局限性，该项分析仍未能得出具体结果，仅给出有动物胶和植物胶存在的初步结论。

3.3.3 彩绘损坏原因研究

彩绘损坏原因是在于对彩绘层破坏形式和在不同条件下(彩绘自身状况和环境状况)的破坏的观察结果。其主要原因是老化的漆层底在防水干燥过程中发生严重收缩，造成裂纹，起翘或卷曲造成的。其次由于原有颜料调和剂老化或流失，颜料层结构变得松散，干燥时易于碎裂。此外，可能还与制作工艺、气候条件、环境条件有关。

3.4 彩绘加固保护的实验研究

寻找适当的保护措施，阻止彩绘剥落一直是秦始兵马俑彩绘保护中重点探讨的问题。中德合作以来，针对这个课题进行了大量的试验研究，使实验一步一步地取得成功。中德合作彩绘加固问题方面的研究可分为下列四个阶段：

第一阶段(1992年-1993年)

这一阶段首先试验了各种加固剂加固彩绘的稳定性，有研究将彩绘调和时，可能防止氧化和光泽的彩绘的剥落，而对生漆层彩绘和生漆层上带有微量颜料层彩绘、这种只通过涂刷加固剂的方法，是达不到防止彩绘剥落目的。彩绘在干燥期间，很可能会有严重的剥落。由于彩绘修整时是在彩绘片上未干时才发生的。彩绘只是一次彩绘彩画片从高湿度环境中移到干干燥的环境下，生漆层快速失水，引起颜料层起翘、卷曲，从而不同其上的颜料层一起从陶底上剥落。于是，采用下列不同的干燥方式进行了对比试验：

2.1.2 一步干燥法，先将经过处理的彩绘彩画片，逐次置于由不同盐溶液控制的湿度系列恒温器内，让其在环境湿度逐步微小降低的条件下缓慢失水，以减小彩绘片失水时的表面张力和生漆层的收缩、变形等现象。

2.1.3 二步干燥法，先于20℃以下进行预干，然后在干燥机内进行干燥，以便彩绘彩画片的内含水分通过升华方式散出，防止底层变形、剥落。彩绘彩画片的内含水分从表面蒸发变为其它覆盖物进行蒸发，以减少彩绘彩画片的干燥速度和避免内含水分从表面蒸发时对脆弱的彩绘造成破坏作用。试验了包扎干燥法和沙浴去湿法。

以上这些试验结果均未能防止生漆底的起翘、剥落和
题。对病因调查发现：1）加固料难以渗透过生锈底层而进入原表面部分，只能通过底层边缘浸入少量加固料，加固强度不足；2）生锈底层干燥时产生严重收缩，浸入加固料的部分，产生许多裂纹，甚至出现起鼓现象；在未加固住的部
分，易发生重点腐蚀或凹陷。

实验结果表明：非水溶性加固料不宜用于粉刷墙面的加固，因其不能使起鼓或卷曲的底层恢复原位或弹平，并防止二次加固处理；比较好的加固料是水性的分解剂和聚丙烯酸

第二阶段（1995年）

基于第一阶段的实验研究结果，这一阶段的加固试验工作主要集中在探讨各种预处理剂对底层性能改善效果的研究上。该项工作分两种情况进行了试验研究。首先选用一系列
试验剂在生锈底层上进行试验，选用了试剂被认为可能
具有下列性能：（1）能均匀分布在表层表面而产生张力力比水小；（2）浸入底层后，将其在内部形成致密结构，起到
目的和填充底层，减小底层干燥时的裂缝；（3）具有显著的干粉层内含水分扩散或吸收的性能，达到减缓干燥的作用；（4）具有提高的性能。方法是：将底层面层直接浸入稀释或未稀
释的试剂中，数天之后，取出展平在玻璃片上，通过视频全息摄影技术测量，记录处理剂对底层性能的认识情况，并
进行外部检查。结果表明，未处理的底层面层干燥度变化
（94.5%-95.5%RH）的底层变形量是13微米，而用叔丁醇
处理过的底层变化的变形量是2微米，用甲基三甲基氧硅烷
处理过的变形量是3微米；用PEG200处理过的变形量为1-3
微米等。由此得出，由于底层表面进行适当处理能够提供较
好的保护效果。

为了使该项实验更接近实际情况，又在彩绘陶片上进行了
试验，方法是先用试剂进行预处理，然后再进行加固，或
是在加固剂中加入一定量的试剂，结果表明：用加有少量
PEG200的加固剂处理过的彩绘陶片，其彩绘层可以保持
稳定干燥的时间。从而表明PEG200具有改善底层在干燥期
间的行为的作用。

第三阶段（1996年-1997年）

由于在前两个实验中，在加固层中加入少量PEG200
获得了较好的保护效果，所以，这一阶段的工作继续在寻找
适当的防止底层收缩的方法上，考虑到在木材保护处理上
施用的逐步处理法，以及通过浸渍渗透方法可以使加固剂更
深更多地浸入到彩绘层和陶质地基中，本项实验采用
PEG200和一些保护效果较好的加固剂进行了多
种试验。结果表明：用PEG200作防收缩剂，聚氨酯乳液或
聚丙烯酸乳液作为加固剂，通过逐步浸渍PEG200
溶液，并于第一阶段加入加固剂溶液的分步处理法，具有钝化
底层对环境湿度变化的敏感性和稳定底层的显著作用，可
避免底层在自然环境下很快变形、剥落的问题。经过这种方法
处理过的彩绘陶片，在室内环境下已放置了两年多时
间，彩绘层仍未变化（图1.4）。而陶片长时间处于潮湿
状态下，带裂纹和颜色加深。试验结果表明，这主要是由于PEG200
具有强烈的吸湿性和很好的蒸气压，从而提高了彩绘陶片内水分朝
外扩散的速率，使陶片在相当长时期内有较多水分的缘
故，推测经过长期缓慢扩散以后，陶和彩绘层的颜色将会恢
复到自然状态。

第四阶段（1998年）

鉴于经过PEG200处理过的彩绘陶片长期处于潮湿状
态，推测可能对兵马俑的修复和长期贮存构成影响。另
外，由于生锈层的难湿透性，如何在达到有效加固强度的
情况下，避免加固剂在彩绘表面的积累，保持其自然的外观状
态。这些问题成为本阶段研究工作探讨的重点。该阶段首先对
经PEG200处理过的彩绘陶片进行了环境湿度变化与其
反应情况的试验。结果表明：用PEG200溶液通过浸渍法处
理过的彩绘陶片，在处于相对湿度约75%以上的环境
下，强烈吸水空气中的水分，表面出现PE200的水
滴。此时彩绘仍主要以陶片结构内渗入量大约PEG200的
原因。于是，采用了不同配方，不同步骤的浸渍渗透法进行
了一系列的试验，取得了下列实验结果：

（1）直接将PEG200试剂进行浸渍处理，会导致生
锈层发生严重起鼓、卷曲。推测这是由于具有强烈吸湿性的
PEG200很快吸水生锈层结构内部水分，导致其迅速脱
水的原因。

（2）用PEG200处理液中不可加入较大的加固剂组
分，否则加固剂会彩绘表面成膜而发亮。使用的加剂数量为
加固剂的固体含量在2%以下，并需采取第一步中加入的
方法。

（3）一般采取下述步骤浸渍处理较好：第一步：聚氨酯
乳液：PEG200水：5-3005；第二步：PEG200水：60-40；第三
步：稀PEG200。每步处理时间为1-2天，需在陶片湿润状
态下进行处理，当陶片较干燥时，处理前应先用水喷
湿，否则，加固剂会在表面成膜，影响外观。

另外，为了检验陶片经过PEG200处理以后，是否对彩
绘有影响其粘结修复性能，用模拟陶片进行了试验。结果表明：处
理过的时间应控制在粘结技术，对初始粘结强度也基本没有
影响。

期间，还积极探讨，以寻找其他更佳的加固方法。采用
易干燥的小分子量单体材料（PLEX6803-10），通过进一步
的步骤处理法，使单体渗入彩绘层和陶表层，从而利用
电子束试内部收集，取得了加固强度和外观状态均很好的
保护效果（图1.4）。

4. 结论

兵马俑彩绘保护课题组，经过大量分析、试验，明确了彩
绘颜色的成分、彩绘的有机底层层是由生漆制作的；详解了彩绘
的剥落机理；基本找到了防止螺纹上残存彩绘剥落的加固方
法。这为以后进行兵马俑彩绘的保护工作奠定了良好的技术
基础。兵马俑彩绘保护是一项系统工程，不仅仅是把
彩绘固定在残片上，还需要将处理过的残片恢复成完整的彩
绘俑，并使其得到长久妥善保存。另外，发掘期间，防止脱落
的彩绘层剥离陶基础而粘于陶土，以及如何将一些粘于
填土上的彩绘恢复到原来陶的位置上，等等。这些问题都需
要今后给予足够关注，并进行积极探讨。
Review of the Conservation of the Polychromy of the Terracotta Army

The polychromy on the 8000 terra-cotta warriors, which were originally coloured from head to toe has largely fallen off due to artificial and natural causes. The remains of the paint layers are very sensitive and react extensively when excavation takes place. Extensive research and work have been done in China and Germany to protect the valuable pigments that remain. Much headway has been made in this respect. This paper gives, from a technological angle, a stage-by-stage review of the colour preservation and the progress made on the research of the polychromy of the warriors since their excavation. It includes components of their colouring, coating technology, causes of the damage and techniques for the protection from the environment. It also mentions some problems, which need further investigation. See colour plate 1.
秦俑彩绘保护研究的新进展


1. 前期研究简介
秦俑彩绘的层次结构类型，目前所观察到的情况，可粗分为两类，细分为六种：

- 纯有机层 (主要成分生漆)
- 单漆层
- 双漆层
- 单漆层 + 单颜料层
- 单漆层 + 多颜料层
- 双漆层 + 单颜料层
- 双漆层 + 多颜料层

以上各种层次结构类型均含有主要成分生漆的有机层，这是秦俑彩绘的重要特点之一。

我们对其分目的无非是两个：一个是对秦俑彩绘工艺，更重要的是考虑对其保护，那么从保护的角度考虑：纯有机层和较厚有机层+很薄的颜料层保护难度大于其他类型。相对来说，有机层越厚越难保护，颜料层越厚越容易保护，这是因为颜料脱落主要是有机层失水收缩造成的，有机关层越薄收缩应力越大。颜料层对底层有一定的壁面作用，从而减缓外界对底层的影响。底层失水速率减慢，收缩变缓。

1.1 分析了彩绘的物质组成

彩绘颜料一般都是无机矿物质颜料。单色颜料成分见下表，其它间色颜料是由两种或多种颜料混合而成。

<table>
<thead>
<tr>
<th>颜色</th>
<th>成分</th>
</tr>
</thead>
<tbody>
<tr>
<td>红色</td>
<td>HgS, PbCO3</td>
</tr>
<tr>
<td>黄色</td>
<td>As2O3</td>
</tr>
<tr>
<td>绿色</td>
<td>CuCO3(OH)2</td>
</tr>
<tr>
<td>蓝色</td>
<td>Cu(CO3)2(OH)2</td>
</tr>
<tr>
<td>紫色</td>
<td>BaCuSiO4</td>
</tr>
<tr>
<td>白色</td>
<td>Ca3(PO4)2OH, PbCO3</td>
</tr>
</tbody>
</table>

有机层或底层的主要成分为中国生漆。

1.2 查明了彩绘脱落的主要原因

颜料粒间之间的粘附力很低，特别是底层(生漆层)对水非常敏感，在干燥过程中漆层急剧收缩，引起漆层起皱纹，造成彩绘脱落(图 1, 彩图 II 1-2)。

1.3 试用过多种物理方法，结果证明对漆层脱水均不适用。

1.4 试用过多种加固方法，未获得理想效果。如单一加固剂加固，加固剂中加入一定量硬化剂等等。

2. 1996-1998 的研究思路
经过近十年的探索，进行了大量的试验之后，为何还不能对彩绘实施有效地保护呢？对此，我们对以往的实验进行了认真的反思和总结，认为彩绘是脱落、损坏的原因，难得出：保护彩绘的关键是稳定漆层。根据秦俑彩绘中漆层的特性，保护方案应包含加固和抗收缩两个方面的处理。

为此，我们设想了以下两个途径：

（1）采用具有抗收缩作用的材料置换漆层中生漆，代替生漆处理，同时采用合适的加固剂加固。

（2）用单体浸入漆层中置换水，经渗透至漆层到漆层与陶体之间，然后设法引发单体交联聚合，聚合物在漆层中减弱收缩，漆在漆层与陶体之间起加固作用。

按照这些思路，安排了以下试验。
3. 保护实验之一

3.1 抗皱缩剂的对比实验
为了找到合适的抗皱缩剂和方法，开展了这项模拟实验，本实验对可能有抗皱缩效果的21种试剂进行了对比实验，其中有4种试剂及方法给出了很好的抗皱缩效果。

3.1.1 试样
为了使这项模拟实验的结果尽量接近真实情况，我们选取了已经脱离体的原始生层面作为试样，它们色泽、厚度的大小约为0.5 x 0.5mm。

3.1.2 试样处理
对所有的试样分别用相应的抗皱缩剂采用浸润或滴加湿润的方法进行处理，处理方法和试剂见表2。

Table 2: Materials and treatment methods.

<table>
<thead>
<tr>
<th>No.</th>
<th>Treatment Agent</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Glycerin / Water</td>
<td>soaking: 30 % 5d; 60 % 7d；80 % 10d；100 % 10d</td>
</tr>
<tr>
<td>A2</td>
<td>PEG 400 / Water</td>
<td>soaking: 30 % 5d; 60 % 7d；80 % 10d；100 % 10d</td>
</tr>
<tr>
<td>A3</td>
<td>PEG 200 / Water</td>
<td>soaking: 30 % 5d; 60 % 7d；80 % 10d；100 % 10d</td>
</tr>
<tr>
<td>A4</td>
<td>D-mannit / Water</td>
<td>soaking: 30 % 5d; 60 % 7d；80 % 10d；100 % 10d</td>
</tr>
<tr>
<td>A5-1</td>
<td>Phenol / Water (1st step)</td>
<td>soaking: 5 % 9d；10 %；16 %</td>
</tr>
<tr>
<td>A5-2</td>
<td>Formaldehyde (2nd step)</td>
<td>soaking: 90 % 5d</td>
</tr>
<tr>
<td>A5-3</td>
<td>Acetaldehyde (3rd step)</td>
<td>gas over solution (30 %) 10d</td>
</tr>
<tr>
<td>A6</td>
<td>Triethanolamine</td>
<td>soaking: 10d</td>
</tr>
<tr>
<td>A7</td>
<td>Gloyxal / Water 40 %</td>
<td>dripping</td>
</tr>
<tr>
<td>A8</td>
<td>hygroscopic Salt: LiCl / Water</td>
<td>dripping</td>
</tr>
<tr>
<td>A9</td>
<td>PEG 200 / DAP 80:20</td>
<td>dripping: saturated solution</td>
</tr>
<tr>
<td>A10</td>
<td>PEG 400 / DAP 80:20</td>
<td>dripping</td>
</tr>
<tr>
<td>A11</td>
<td>PEG 1500 / DAP / Water 66:17:17</td>
<td>dripping</td>
</tr>
<tr>
<td>A12</td>
<td>1,3-Propylaminum-dichloride (PAD+HCl)</td>
<td>dripping</td>
</tr>
<tr>
<td>A13</td>
<td>MEG (ethylen glycol) / Water</td>
<td>soaking: 30 % 7d; 60 % 10d；80 % d；100 % d</td>
</tr>
<tr>
<td>A14</td>
<td>pre-PMMA / Acetone, 50:50</td>
<td>dripping</td>
</tr>
<tr>
<td>A15</td>
<td>n-Hexadecylammonium-chloride /</td>
<td>soaking</td>
</tr>
<tr>
<td></td>
<td>Acetone+ Water (20:80)</td>
<td></td>
</tr>
<tr>
<td>A16</td>
<td>Colophonium / Acetone 1:2</td>
<td>dripping</td>
</tr>
<tr>
<td>A17</td>
<td>Tetramethylammonium-hydroxide /</td>
<td>dripping</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>A18</td>
<td>Tungoil (300 C) / Ethylacetate</td>
<td>soaking</td>
</tr>
<tr>
<td>A19</td>
<td>Tungoil / Ethylacetate</td>
<td>soaking</td>
</tr>
<tr>
<td>A20</td>
<td>PEG 1500 + Glycerin 1:1</td>
<td>soaking</td>
</tr>
</tbody>
</table>
3.1.3 评估
所有评估项目都是在显微镜下观察评估的。评估项目的
主要关注点为抗皱缩效果。底层漆层的厚度变化、抗皱缩能力
的持久性等等。评估内容选择是根据彩绘保护的实际情况而
定的。处理后的外观也应作为重要的评估内容之一。然
而，由于漆层厚度是深棕色的，处理后色调的变化情况难以
分辩，因而这一重要的评估内容在这个初步的实验中没有进
行。所有内容在进行的彩绘保护的实验中进行了详细的
研究。
抗皱缩项目的评估方法如下：首先选用低吸水处理过的漆
片表面的残余液，然后观察漆片是否平展。再给漆片表面滴
加水并观察其形状是否有变化。如果处理后不平展、而且
滴水后其形状发生了变化，说明处理剂及其处理没有抗皱缩
效果，这样我们便给出“+”符号；相反地，说明该处理
方法和处理剂有抗皱缩效果，便是“+”符号。利用这种
现象，作为评估的依据是基于彩绘漆层对水的反应特
性。秦俑彩绘漆层在其含水量的变化过程中会引起其形
状的剧烈变化，(见秦俑彩绘保护项目 1994 年度研究所
告)这种形状的剧烈变化即所谓的皱缩。

腕性变化项目的评估：
先使处理后的漆片表面干燥，方法如前项所述。然后
利用小镊子轻触漆片的，未处理的小漆片，再分别轻触各组已
经处理过的漆片，并相互比较其腕性。如果腕性相似，便
是“+”符号。如果某个处理后的小漆片腕性被认为高于对照
样，则是“-”符号。其他情况则为“+”符号。

长期效果的评估：
处理后的漆层的抗皱缩效果持久性如何以及处理剂蒸
发后曾被增强的抗皱缩性的底层有什么变化也是我们所
关注的问题之一。为此，我们也设计了这项评估，评估方法
如下：处理前的漆片在表面，再给漆片表面滴加丙酮，仔细观察小漆片的变
化直至丙酮完全蒸发，然后给小漆片滴加水并观察之。如果漆片形状发生变
化，则意味着这种试剂的耐久性不好，评估为“+”符号，反之，则为“-”符号。

3.1.4 结果讨论
所有的评估结果见表 3(见 26 页)。

3.2 加固剂的对比实验
该项实验的目的是找到最适合漆层加固的加固剂。根据以往
的测试结果，结合有关资料报导，我们选用了 21 种加固剂
进行对比实验，通过一系列的评估对比筛选出了适合漆层加
固的 3 种加固剂(见 26 页表 4)。

3.2.1 试样
为了使对比实验更接近实际情况，而又不至于用真实彩绘的
彩陶试样，我们选用了已经脱离陶体的原始生漆层碎片作
为试样，它们厚度的大小为 0.5×0.5mm。

3.2.2 对比实验及评估
(1) 加固剂对漆层的对比实验
为了了解不同加固剂对漆层的适应性及加固效果，而安排了
这个实验。

具体做法是：将漆层碎片放在玻片上，滴加加固剂，观
察反应情况，然后对下表项目进行评估对比。

- 是否会引起漆层卷曲
- 是否会形成破碎
- 是否会使颜色
- 产生光泽
- 加固效果如何
- 评估符号

<table>
<thead>
<tr>
<th>卷曲</th>
<th>破碎</th>
<th>加固效果</th>
<th>色泽</th>
<th>光泽</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>+++</td>
</tr>
<tr>
<td>+/-</td>
<td>+/+-</td>
<td>=/=/=</td>
<td>=/=-</td>
<td>=/=</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

对比实验结果见表 5(见 27 页)。

(2) 加固剂在潮湿环境中的对比实验
将现代制作的彩陶放入相对湿度为 84 %RH(原始彩陶彩
片在保护前的近似值)的环境内至不再增重，涂刷加固剂于潮
湿彩陶上观察结果(见 27 页表 6)。

(3) 各种加固剂在玻片上的对比实验
将加固剂涂在玻片上，干燥后观察其结果(见 27 页表 7)。

综合以上三项试验结果，可以得出以下结论：加固剂 C1 的
综合性能和对漆层的适应性最好，其次为 C5b 和 C12 等等。

3.3 在真实陶片上的实验

3.3.1 抗皱缩实验
虽然 PEG 2000、PEG 4000、甘油对漆层都有较好的抗皱缩效
果，但甘油容易在彩绘表面形成一层粘稠的物质，PEG 4000
粘度明显大于 PEG 2000，因此，选定 PEG 2000 作为彩绘保护
的抗皱缩剂。

处理方法：用浸渍方式，PEG 2000 溶度逐级升高
(40、60、80、100 %)每小时为 15 分钟，

处理彩绘的残片 F-005a/96 和 F-003/ 96

彩图 II, 3. 陶片 F-003/ 96，处理后。

该陶片曾用 PEG 2000 经过逐级提高浓度包敷处理，然后
在适宜的室内环境中暴露了 4 个季节，其甲带上的红色颜料
层与底层粘附良好。颜料层有部分损失。大多数甲带上的漆
Table 3: Evaluation result: A1 = A3 > A2 > A7 > A13.

Table 4: Consolidation agents.

<table>
<thead>
<tr>
<th>No.</th>
<th>Consolidation Material (from Sichuan)</th>
<th>Solvent</th>
<th>PH</th>
<th>No.</th>
<th>Consolidation Material (from Sichuan)</th>
<th>Solvent</th>
<th>PH</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Polyurethane dispersion (Kremer 7680)</td>
<td>Water</td>
<td>5-6</td>
<td>C12</td>
<td>Butylmethacrylatelatulsion (Motema WPC)</td>
<td>Water</td>
<td>6-7</td>
</tr>
<tr>
<td>C1b</td>
<td>CI in Ethanol 1:2</td>
<td>Water / Ethanol</td>
<td>7-8</td>
<td>C13</td>
<td>Bologna-Cocktail</td>
<td>Xylene / Acetone</td>
<td>7-8</td>
</tr>
<tr>
<td>C2</td>
<td>Colophonium + Acetone 1:2</td>
<td>Acetone</td>
<td></td>
<td>C14b</td>
<td>Beeswax C14 (fine) / Dispersion (Ultrasonic)</td>
<td>Water</td>
<td>7-8</td>
</tr>
<tr>
<td>C3</td>
<td>Lacquerum + Glycerine</td>
<td>Water</td>
<td>5-6</td>
<td>C15b</td>
<td>Urushiol C 15</td>
<td>tBuOH</td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td>Polymethylmetacrylatulsion 1:2 (Primal AC 33)</td>
<td>Water</td>
<td>7-8</td>
<td>C16</td>
<td>C14b + C13b / Beeswax (Ultrasonic) + Polyurethane (in Ethanol) 1:3</td>
<td>Water</td>
<td>7-8</td>
</tr>
<tr>
<td>C5b</td>
<td>Primal AC 33 in Ethanol / Dispersion</td>
<td>Water / Thanol</td>
<td>7-8</td>
<td>C17</td>
<td>Acrylkleber (48 %) + Ethanol 1:9 (Kremer 360 HV)</td>
<td>Ethanol</td>
<td></td>
</tr>
<tr>
<td>C7</td>
<td>Polycrylatulsion 1:2 (Motema Finish)</td>
<td>Xylene</td>
<td></td>
<td>C18</td>
<td>Plexisol P 550 40 % (42 %) + White Spirit 1:2</td>
<td>White Spirit</td>
<td></td>
</tr>
<tr>
<td>C7b</td>
<td>Molema Finish + tBuOH</td>
<td>tBuOH</td>
<td></td>
<td>C19</td>
<td>Paraloid B 72 9 % + MTMOS 7 % in tBuOH</td>
<td>tBuOH</td>
<td></td>
</tr>
<tr>
<td>C8</td>
<td>Wacker Steinfestiger OH</td>
<td>Ethyl-Acetate</td>
<td></td>
<td>C20</td>
<td>Shellac (in Borax-solution)</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>C9</td>
<td>BCP (Bologna-Cocktail) + PEG 200</td>
<td>Organic</td>
<td></td>
<td>C21</td>
<td>Water-based Epoxy-Resin-Dispersion (Sikaflour 2520)</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>C10</td>
<td>Polyacrylate-microparticle-dispersion</td>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Rolling</td>
<td>Cracks</td>
<td>Adhesion</td>
<td>Colour</td>
<td>Gloss</td>
<td>Conclusion</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>---------</td>
<td>--------</td>
<td>----------</td>
<td>--------</td>
<td>-------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>very good</td>
<td></td>
</tr>
<tr>
<td>C1b</td>
<td>+/-</td>
<td>+</td>
<td>+/-</td>
<td>+</td>
<td>+/-</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>+</td>
<td>+/-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>bad</td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td>+/-</td>
<td>--</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>bad</td>
<td></td>
</tr>
<tr>
<td>C5b</td>
<td>+/-</td>
<td>--</td>
<td>+</td>
<td>+</td>
<td>+/-</td>
<td>ordinary</td>
<td></td>
</tr>
<tr>
<td>C7</td>
<td>-</td>
<td>+</td>
<td>+/-</td>
<td>+</td>
<td>+/-</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C7b</td>
<td>+/-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+/-</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C8</td>
<td>+/-</td>
<td>-</td>
<td>-</td>
<td>+/-</td>
<td>-</td>
<td>very bad</td>
<td></td>
</tr>
<tr>
<td>C9</td>
<td>-</td>
<td>+/-</td>
<td>+/-</td>
<td>+</td>
<td>+</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C10</td>
<td>+</td>
<td>-</td>
<td>+/-</td>
<td>+</td>
<td>-</td>
<td>ordinary</td>
<td></td>
</tr>
<tr>
<td>C12</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C13</td>
<td>+/-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>ordinary</td>
<td></td>
</tr>
<tr>
<td>C14b</td>
<td>+/-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>(some white)*</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C15b</td>
<td>+</td>
<td>+</td>
<td>--</td>
<td>-</td>
<td>-</td>
<td>very bad</td>
<td></td>
</tr>
<tr>
<td>C16</td>
<td>+/-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>bad</td>
<td></td>
</tr>
<tr>
<td>C17</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>bad</td>
<td></td>
</tr>
<tr>
<td>C18</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>very good</td>
<td></td>
</tr>
<tr>
<td>C19</td>
<td>+/-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+/-</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>C20</td>
<td>-</td>
<td>-</td>
<td>+/-</td>
<td>+</td>
<td>-</td>
<td>very bad</td>
<td></td>
</tr>
<tr>
<td>C21</td>
<td>-</td>
<td>+/-</td>
<td>-</td>
<td>+/-</td>
<td>slowly**</td>
<td>bad</td>
<td></td>
</tr>
</tbody>
</table>

Table 5: Comparison tests on the separate ground layer flakes.
* : The colour of the lacquer flake was slightly white.
**: The epoxy-resin hardens very slowly.

由上表可以看出：该实验结果最好的是 C1 > C18 > C7b

Table 6: Conclusion of the experiments on damp terracotta pieces.
C3 > C1 = C5b = C9 = C13 = C14b = C20

Table 7: Conclusion of the experiments on glass pieces.
评估结果：C1 = C2 = C5b = C12 = C19
优化的方法为：
第一步：使陶片处于饱和状态。
第二步：RuPGE200: H₂O=2.5: 30: 67.5, 2 天
第三步：PGE200: H₂O=60: 40, 2 天
第四步：纯 RuPGE200, 1 天
用这种方法处理一批彩绘陶件，已经在自然室内环境中暴露出 4 个多月，保护效果良好。

3.4 结论
(1) 通过对彩绘彩绘中的彩层、蛋乙醇(PEG)和具有良好的抗蚀性。
(2) 在一系列表面实验中，我们发现若用一种纯的浸没剂与彩层浸渍接触，彩层中的水分与该浸没剂的置换不协调，这种情况下彩层会退色和卷曲，与彩层自然干燥的现象相似。根据彩层对水的反应特征，只有通过逐步升高抗蚀剂浓度的方法，置换过程才可以安全进行，用这种方法处理彩绘陶件，实现了彩绘陶件中水分与抗蚀剂的自然安全交流。
(3) 平均分子量为 2000 的 RuPGE200 在饱和度和饱和度稳定性方面表现出了良好的效果。同时，与加固剂联用时也表现出了最好的协同效应。
(4) 两种化学结构不同的聚合物乳液在联用保护处理中产生了相似的加固作用。相比之下，聚氨酯(PU)乳液(Kemer 7680)比聚丙烯酸酯乳液(Motema WPC)有更好的加固效果。
(5) 经过这套保护方法处理过的彩绘陶片的已经在临沧的自然室内环境中暴露了 2 年多，最短的也已经暴露了近 4 个月，这些彩绘彩绘色彩良好，彩层仍保持稳定。因此可以认为这套保护方法已经实验在实验室取得了成功。

4. 单体渗入，引发聚合的保护实验
1997/96 年度便开始的这项实验，在对 20 多种单体进行聚合性能的模实研究后，选择出了适用的单体，（一种可以用于水的甲基丙烯酸甲酯）。对于引发剂、UV 光引发等多种方法的实验，选定了电子束(EB)辐射引发聚合的方法。该方法处理过的彩绘陶片，达了理想的保护效果(详见 Rohner 的报告，彩图 III, 13)。目前，我们已在深圳附近找到了这种仪器设备，即将开展进一步实验研究，以完善这种保护方法。

5. 总结
经过几年努力，我们初步完成了几年提出的实验思路，在两条重要的保护途径上，均获得了成功。但这只是实验室阶段成果，还有许多问题需要深入研究，要将这些成果转化为实际应用的保护技术还要做大量工作。
Fig. 1. This set of five photos shows the movement of the lacquer layer during the drying process. This lacquer layer has peeled off from the terra cotta was taken from a box (100% RH) to an open room (60% RH). It happened in four minutes. (Photos: Cristina Thieme)
1: The phase of the beginning: 100% RH; 2: The phase after 1 minute, under 60% RH; 3: After 2 minutes; 4: The phase after four minutes; 5: After five minutes

图 1. 这组 5 张照片是对湿度变化非常敏感的漆层在干燥过程中发生的运动。这块漆片(已从陶体上脱离)从相对湿度 100% 的保湿箱中取出，放到 60% (RH) 的室内环境中，反应过程为 4 分钟。(摄影: 蒂美)
1) 湿度 100%(RH)时的初始状态; 2) 湿度 60%(RH) 下，一分钟后的状态; 3) 两分钟后; 4) 两分半钟后; 5) 四分钟以后的状态。
New Developments in the Conservation of the Polychromy of the Terracotta Army

This paper (see colour plates II, III) is on the progress of research on the conservation of the polychromy of the terracotta warriors which was carried out by the Museum of the Terracotta Warriors, and the Bayerisches Landesamt für Denkmalpflege. A large amount of work has been done on this project:

1. The structure of the paint layer was investigated.
2. The components of pigments were analysed. Chinese lacquer was considered the main component of the ground layer.
3. The key reasons for the polychrome damage were discovered: the adhesion of the pigment particles to one another is very weak; especially the ground layer is very sensitive to the loss of water. It shrinks extensively when drying, causing a detachment of the ground layer from the terracotta base and a rising of the pigments.
4. Several physical drying-methods were tested, but were proved not fit for conservation.
5. Various methods of consolidation were tested, but not found appropriate.

Based on previous research, the key to the conservation of the paint layers is to steady the ground lacquer layer. The conservation methods for the polychromy of the terracotta must include two aspects: the paint layers should not shrink and must be consolidated.

Applying a monomer to penetrate into the ground layer, so that a polymerised reaction can take place, the consolidation between the lacquer layer and the terracotta base ensues. The following two experiments were carried out from 1996-1998.

1. 21 consolidation agents and 19 agents preventing shrinkage were tested and evaluated. Polyurethane dispersion (PU) and PEG 200 (anti-shrink) were considered as better conservation shrinkage prevention agents. Some original fragments with polychrome layers were treated stepwise with PEG 200 and PU dispersion after application of the last treatment step (100% PEG 200). The fragments could be exposed to the environment for two years and the stability of the preserved polychrome layers did not change.
2. 20 monomers were tested. By means of these experiments, suitable monomers were determined. Various polymerising methods were tested (such as starter UV, etc.) The EB polymerisation method was finally selected, the fragment was treated with the monomer PLEX 6803-20 (water-soluble acrylic ester) and EB polymerised. It showed perfect results.
Methods in Organic Archaeometry and their Application to the Terracotta Army

Introduction

Since the 1950s, the application of science to the study of the past is named archaeometry. The main tasks of archaeometry are prospection, material analysis and dating. The scientific results ought to be discussed in the context of and together with the disciplines that ask the questions, e.g., archaeology, art history and conservation. This presentation tries to give a survey of methods for organic archaeometry. In this sense, organic archaeometry means the application of scientific methods to organic archaeological objects or residues. These materials mostly originate from natural products, such as oils and fats, waxes, bituminous materials, carbohydrates and cellulosic materials, proteins, natural resins and dyestuffs. Chemical analysis reveals the composition of a given material and in most cases either serves the identification or the preservation of an archaeological or artistic object. The classical chemical analysis must be considered outdated and its application to objects of archaeology and art should be avoided. Particularly for organic chemical analysis a too large amount of sample material is required. On the other hand, the exactness of the results is generally low. Similar to infrared spectroscopy, only groups of substances can be found. It is useful to divide instrumental methods for organic analysis into spectrometric identification and substance separation by chromatography. The most prominent methods are shown in fig. 1 together with a very general view over the field of application in archaeology and art.

<table>
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The need of isolated samples is a common characteristic of the majority of organic analytical methods. In the case of the investigation of valuable archaeological and art historical objects of course, this is a severe disadvantage. However, many methods nowadays require only tiny samples of some nanograms, an amount which can hardly be seen by the bare eye. Thus, the sampling technique is the most important step of analysis, when the care of the object is concerned.

Some of the methods discussed here have been applied to problems of the Lintong Terracotta Army in the joint research programme by a number of collaborators. An overview of the results is given here. The investigations focused on the ground layer of the polychromy. This paint layer was found to be mainly responsible for the conservation problems of the polychromy on the Terracotta Warriors, due to its extreme sensitivity to changes in humidity. Some of the scientific results of the joint research programme are published in greater detail elsewhere.

Microscopy

Optical Microscopy

Light microscopy was probably the first technical tool for investigating works of art and archaeology. It is yet today an important method. By light microscopy magnification up to 1500 times is possible. Transmittant illumination techniques as well as top light illumination are commonly applied in the arts and archaeology, using a great number of different technical setups and certain optical effects.

Identification of Fibre and Wood

Polarised light microscopy is a well known transmittant illumination method for the identification of pigments. Furthermore, fibres exhibit optical effects under polarised light as well. These can be used to identify natural fibres from plants as well as from animals. Transmittant light microscopy is also used for botanical identification of wood which is prepared as a thin section.

Application

The Terracotta Army was set up in a giant wooden underground construction. Most of the timber has rotted or been charred. The determination of the tree species from which the timber was produced is of interest for archaeological studies. Two charcoal pieces and two samples of rotted wood from excavation pit no. 2 were botanically determined, as shown in fig. 2. Surprisingly, the charred samples revealed different types of wood. Obviously not much attention was paid to the origin of the wood during construction work.

Stratigraphy

Samples from the surface of an object are commonly prepared as cross sections. In order to investigate their layer structure the polished cross section is examined under the top-light microscope. Some of the layers may appear bright in ultraviolet light due to fluorescence.

Application

The stratigraphy of the polychrome painting layers of the Terracotta Warriors was examined by top light illumination microscopy. Under visible light the ground layer on the Terracotta Warriors looks rather dark and dense. Under UV-light the lacquer exhibits only a weak, greenish-yellow fluorescence.

Fig. 3. Cross section of ground layer on Terracotta Warrior under UV-light (photo: Cristina Thieme).
However, here two layers with a total thickness of about 0.1 mm can be recognised (see fig. 3.). Furthermore, the microscopical picture shows a lot of holes and pores in the dried-out ground layers. In contrast, other examined ground layer samples possess a more dense structure and sometimes also only one layer.

**Scanning Electron Microscopy**

**General**

Scanning electron microscopy (SEM) is known as a powerful tool for looking at tiny samples. In the field of art and archaeology magnification up to 10'000 times are common. The particular advantages of SEM cover the field of inorganic material, including elementary analysis. Further advantages of this technique are high magnification and resolution of the topography. Whereas the usual SEM needs totally dry samples, cryo-SEM is capable to visualise damp structures and even water itself. "Cryo" means that sample preparation as well as microscopy are carried out at very low temperatures. Before introducing it into the microscope, the damp sample is shock frozen in melting nitrogen at -210 °C. This allows the water content to solidify into an amorphous state, so that the damp structures are preserved. The investigation itself is carried out at temperatures far below 0 °C, where the partial water vapour pressure lies below the working pressure of the microscope.

**Application**

Original ground layer samples from the Terracotta Warriors were investigated with cryo-SEM in order to visualise the microstructure of water soaked specimens in comparison to those in dry condition. Fig. 4 shows a double ground layer in damp condition. Two layers can be clearly seen. They exhibit a dense structure and typical brittle fracture forms. Under higher magnification micropores with diameters below 0.1 μm were visible.

Subsequently the cooling of the SEM chamber was stopped and the sample thus dried under the high vacuum. This process led to a total collapse of one of the layers (see fig. 5). This behaviour could probably explain the rolling of the ground paint during drying although this process was much more extensive than under normal pressure. In the remaining layer bigger cavities with diameters above 10 μm have formed. This appearance of the layers closely corresponds to the structure of the air dried ground layer (see fig. 5).

**Spectrometry**

**Introduction**

Spectrometry is in general based on the interaction of electromagnetic radiation with the analysed material. Radiation can lose intensity by absorption, reflection, or scattering. A wide range of the electromagnetic spectrum is used for analytical methods. The high energy x-rays are not suitable for organic analysis, but are very useful for elementary analysis by x-ray fluorescence (XRF) as well as for x-ray pictures. For the identification of dyestuffs the choice method is ultraviolet-visible spectrometry (UV/vis). Infrared spectrometry (IR) uses radiation of lower energy than visible light. It is applicable to inorganic as well as to organic substances. The range of radio waves is used for nuclear magnetic resonance spectroscopy (NMR). In this case a magnetic field has to be additionally applied. In a more general sense, the distribution of particles with respect to their mass can be regarded as spectrometry as well. This principle is used in mass spectrometry (MS).
Infrared Spectrometry

General

Infrared spectrometry is based on the absorption of infrared radiation by the chemical bonds in molecules. In an IR spectrum, the absorption or transmission is displayed as a function of the energy of radiation and noted as "wavenumber" in reciprocal centimetres. IR spectrometry is applicable to detect a wide range of materials. For pure substances information on the precise molecular structure is obtained. On the other hand, mixtures can be generally characterised only according to the functional groups present. Therefore, in general, it is impossible to distinguish resins, oils or proteins more precisely by IR spectrometry. IR spectrometry is particularly capable for the identification of synthetic polymers. Usually the measured spectrum is compared to reference spectra of known substances.

Nowadays mostly Fourier-transform infrared spectrometry (FT-IR) is used. FT-IR made possible the introduction of microscopy to infrared spectrometry. This technique only requires very small samples in the range of 30 micrometers in diameter or about 30 nanograms of mass. Commonly a so-called diamond anvil cell is used together with this technique. The advantages of FT-IR-microspectroscopy are low sample size, rapid data recording and a wide area of application. Because this technique is non-destructive, the sample once taken may be used for further analysis.

Raman spectrometry is closely related to infrared spectrometry. Here, the sample or object is illuminated with laser light and the scattered light is recorded. Sample spectra in the infrared range are obtained. Because the scattered light is registered, this technique does not necessarily require isolated samples. Indeed, Raman spectrometry seems to be the only method up to now revealing information of the organic chemistry of an object without destruction. However, as the Raman effect is very weak, a lot of instrumental problems still have to be solved before Raman spectroscopy can become a routine method of investigating objects of art and archaeology.

Application

In the case of the Terracotta Warriors microchemical test reactions failed in determining the composition of the ground layer. At first by FT-IR it was proved that the ground layer had been prepared from oriental lacquer (Qī-laque). The FT-IR spectra of the two tested ground layers originating from one fragment show a high degree of similarity to one another as well as to the spectrum of the lacquer reference sample (see fig. 6). By investigation of artificial lacquer samples mixed with different binding media, it was found that the determination of additives to oriental lacquer is hardly possible by FT-IR-spectrometry.

NMR

Nuclear Magnetic Resonance Spectroscopy (NMR) is based on the response of certain atomic nuclei to electromagnetic radiation when exposed to a magnetic field. The most important types of nuclides are hydrogen (¹H, proton) and carbon (¹³C). Each particular type of atom or functional group produces a characteristic signal which is expressed as the chemical shift “delta” in ppm. Furthermore, quantitative information can be deduced from an NMR-spectrum.

Proton- and ¹³C-NMR-spectroscopy is mainly suitable for determining the structure of organic molecules. In the field of archaeology and conservation NMR spectroscopy has successfully been applied to the identification of resins and amorbs, waxes, tar and pitch. Furthermore, the state of decay of wood
and bone has been investigated using this method. More generally, this technique was employed to detect the distribution of water or consolidants inside archaeological objects. Advantages of NMR-spectroscopy are simultaneous data acquisition and high resolution in discriminating functional groups. On the other hand, resolution is poor when investigating mixtures. The former disadvantage of NMR, that only liquid samples could be analysed, has been overcome by special measurement techniques. Solid-state 13C-NMR is performed using cross polarisation and magic angle spinning (13C CP/MAS). Compared to 1H-NMR spectroscopy, the sensitivity of carbon-13 is much lower. This requires longer measuring time and relatively large samples of 50 to 250 mg that need to be powdered. For application in archaeology it is a problem that NMR measurements are strongly disturbed by paramagnetic impurities such as iron salts.

**Application**

Original ground layer from the Terracotta Army as well as an artificial lacquer sample were measured by solid-state-carbon-13-NMR. The general shapes of the spectra of both samples are quite similar (Figure 7). This strongly supports the assumption that the ground layer of the Terracotta Warriors consists of oriental lacquer. Differences between the samples can be seen, especially in the content of oxygen-bearing groups (oxygen-bearing aromatic carbons at 145 ppm, carbonyl groups at 175 to 200 ppm). This is attributed to an oxidative weathering of the original lacquer.

**Mass Spectrometry**

Generally, in a mass spectrometer the analyte is transformed into electrically charged particles. These ions are accelerated and separated according to their mass and their electrical charge. The resulting diagram shows the relative abundance of the particles having a certain mass-to-charge-ratio (m/z). It is impossible to present the great variety of MS techniques nor their application on organic archaeometry here. Gas Chromatography e.g. commonly is combined with quadrupol-MS.

In direct temperature-resolved mass spectrometry (DTMS) the sample is vapourised by heating. This method has been introduced to the analysis of resin coatings in the last few years. In contrast to pyrolysis, here the final temperature is reached more slowly, which leads to a separation of low molecular weight parts of the sample from polymeric components. The advantages of DTMS are low sample requirement, short analysis time and no need of sample pretreatment.
Matrix Assisted Laser Desorption and Ionisation (MALDI) is a special method for soft vaporisation and ionisation in MS. It is particularly advantageous for investigation of high molecular and low volatile substances, such as Asian lacquer. MALDI-MS has been applied to some lacquer samples including ground layer of the Terracotta Warriors.\textsuperscript{16}

Chromatography

Introduction

Chromatography is a group of analytical techniques for separation, identification and quantification of substances. The common principle is the migration of the substances on the basis of their different distribution on two immiscible phases. One of these is the stationary phase, the other one is the mobile phase. Depending on the arrangement of the stationary phase, planar chromatography can be distinguished from column chromatography. Planar chromatography was begun with paper sheets, later coated glass plates appeared. Now for analytical purposes mostly Thin Layer Chromatography (TLC) is applied using thin plastic or aluminium sheets covered with a finely grained mineral, mostly silica. Planar chromatography has been applied to art and archaeology for almost 50 years, especially for dyes, polysaccharides, resins, and proteins. This method has been revived today in the form of High-performance-TLC (HPTLC) which is characterised by a very thin stationary phase of extremely fine grained particles.\textsuperscript{17} In the case of planar chromatography, the separated analyte remains on the stationary phase forming a so-called “internal chromatogram”. Each component is characterised by the travelled distance in relation to the front of the moving phase, expressed by the $R_e$-value.

The column chromatographic techniques, actually using a thin capillary, are commonly further classified depending on the nature of the mobile phase. Different techniques of liquid chromatography (LC) as well as Gas Chromatography (GC) and Supercritical Fluid Chromatography (SFC) have been developed.\textsuperscript{18} The column techniques produce external chromatograms, which means that the substances are detected at the end of the column. The resulting chromatogram shows the signal from the detector as a function of time. The characteristic value is called Retention time ($t_r$).

Fig. 8. Ion-exchange-liquid-chromatograms of: a) hydrolysed insoluble part of original ground layer with adherent clay (Q011/95) and b) lacquer reference sample containing pig blood (CL11), (Irene Friedler, Doerner Institut, Munich).

图 8. 离子交换液相色谱图: a) 带有粘土的原始基层(Q011/95)在水解之后的不溶解部分; b) 含有猪血的参照样品(CL11)。
The material being analysed by a chromatographic technique has to move. Therefore it must be either soluble in the case of TLC and LC or volatile in the case of GC, respectively. Natural polymeric materials (proteins, carbohydrates, dried oils) have to be broken down chemically into their low molecular building units – mostly by hydrolysis in aqueous solution.

**Liquid Chromatography**

**General**

Liquid chromatography can be used for the separation of soluble and polar or high molecular substances. High Performance
Liquid Chromatography (HPLC) works with relatively short time spans using high pressure and a thin column. Whereas in the beginning of HPLC the column material was more polar than the solvent, now the most frequently used method is the “reversed phase”-HPLC where the mobile phase is more polar than the column. In the field of archaeometry HPLC is applied to the analysis of amino acids from proteins, dyes, and carbohydrates.

Proteins can be identified by their amino acid composition, which is characteristic for the different types of proteins used as binding media. After hydrolysis of the protein the resulting amino acid mixture is separated and identified by liquid chromatography. A column packed with ion exchange resin is used. In the form of a special “amino acid analyser” this method has been applied to problems in art and archaeology for many years. More recently a HPLC-method for detecting proteins, was described in the literature using special methods of hydrolysis and derivatisation.

Application

Ion-exchange LC was applied to samples of original paint layer of the Lintong Terracotta Warriors as well as to lacquer reference samples in order to detect a possible protein content. It was found that neither the original samples nor the reference contained any water soluble protein components. From the water insoluble residues of two original ground layer samples amino acid profiles were gained, which were similar to that from the lacquer reference sample containing pig blood. This preliminary result hints to the addition of blood to the ground layer painting material of the Terracotta Warriors. Animal glue was not detected in any original sample. However, more original samples as well as different reference material should be analysed in order to confirm this assumption. Contrary to the ground layer, two analysed paint layer samples contained only a few amino acids of low concentration.

Gas Chromatography

General

Gas chromatography (GC) has been used for decades for the separation of mixtures of volatile and low polar components. In this chromatographic technique the moving phase is a gas, while the stationary phase is liquid. In the field of archaeology and art, gas chromatography has been broadly applied to the analysis of most of the organic materials. A common way to make the analyte volatile is to treat it chemically, which is called “derivatisation”. Another possibility of vaporisation is to decompose high molecular materials by heating, which is called pyrolysis (Py-GC). Successful applications have been reported to the analyses of amber as well as fossil bitumens (jet).

In GC the vapourised sample is forced by means of a carrier gas through a long, thin capillary called “column”. The inner surface of the column is filled with the stationary phase, which is a high boiling liquid. Usually, the column is heated. At the end of the column the separated fractions of the sample are registered by the detector. The most commonly used type is the flame ionisation detector (FID). Nowadays, often a mass spectrometer is used as a detector in gas chromatography, as shown below. Like in liquid chromatography, the resulting diagram depicts the time.

Application

In a first step an original sample of the ground layer from the Terracotta Warriors as well as a Han lacquer sample were analysed by GC after conventional derivatisation. Since both samples remained almost completely insoluble only traces of fatty material and of polysaccharides were found without possibility of further identification. This clearly showed that in the case of cross-linked polymers such as oriental lacquer chemical derivatisation is not able to make them volatile.

In the second step pyrolysis gas chromatography (Py-GC) was applied in order to identify the main component in the original ground layer samples as well as in a comparison sample from the Han Dynasty. In fig. 9, the chromatograms of both original samples (“Qin, Han”) show a high degree of similarity to one another and are also in accordance to that of artificial lacquer “CL1”. Thus it can be concluded that both original samples have been produced from oriental lacquer. The original samples showed fewer peaks with lower intensity as compared to the artificial sample. This suggests that the complex network of hardened lacquer has been degraded or perhaps some components have been leached out during the ageing process in the ground.

Meanwhile, the application of Py-GC combined with MS to asian lacquer has been published in the literature (see below).

Hyphenated Methods

Introduction

"Hyphenated techniques" in general means the combination of two or more separate analytical techniques. Because column chromatography requires external detection, it is particularly useful to combine gas or liquid chromatography with a spectroscopic technique such as UV/vis, infrared, mass or nuclear magnetic spectroscopy. Most of the powerful modern analytical techniques are one of these multi-dimensional systems. They usually are connected to a computer to handle the great amount of data.

HPLC-UV/vis

General

Liquid chromatography has suffered from detectors which are either not highly sensitive or not selective. To overcome this disadvantage, LC is commonly combined with other analytical methods. For the detection of organic dyes in objects of archaeology and art ultraviolet-visible spectrometry (UV/vis) is obviously the best method. After having passed the HPLC-capillary the solution is analysed by the diode-array detector (DAD) which repeatedly generates UV/vis-spectra of the separated substances. The results are normally given as liquid chromatograms. Furthermore, for each retention time a complete UV/vis-spectrum is recorded. So each peak in the chromatogram can be identified by its spectrum, which is typical for certain dyes. The sensitivity of this method for organic dyes lies in the range of a few nanograms.
In the case of the Terracotta Warriors HPLC-UV/vis was employed to samples from pink-coloured parts of the polychromy, representing bare skin. This type of paint was supposed to contain organic dyes because it seemed to bleach out upon being exposed to light after excavation. However, it has to be reported that no organic dye was found in the pink paint layer sample under investigation. Therefore the light-sensitive pink tone is generated by the inorganic pigment cinnabar rather than by an organic dye.

Gas Chromatography-Mass Spectroscopy (GC-MS)

General

Probably the most valuable tool for the analysis of mixtures of low molecular weight organic components has become the on-line combination of gas chromatography and mass spectrometry (GC-MS). This is also true for the field of archaeology and art. Numerous investigations of materials from artifacts have been published, including resins, oils, waxes, and proteins. In this system, the gas chromatograph serves as the separation technique, while a quadrupole mass spectrometer is used for the molecular identification of the components. One great advantage of GC-MS is the capability of detecting extremely small amounts of individual substances in complex mixtures — thus it is ideal for archaeological and artistic works. On the other hand, only volatile substances can be analysed directly. This sometimes requires sophisticated methods of enrichment and pretreatment of the substances to be analysed. Furthermore, the resulting mass spectra are often complicated because of fragmentation of the analyte molecules during ionisation.

From the two-dimensional data resulting from GC-MS set the following diagrams can be deduced:

1. Total Ion Current Chromatogram: For each retention time the signal of all m/z are summed up. Here, the MS just works as a detector similar to the conventional column chromatography.

2. Mass Chromatogram: Here, the intensity for a certain m/z value is plotted over the retention time, so that the occurrence ions characteristic for certain compounds can be extracted from the chromatogram.

3. Mass Spectrum: For a given retention time, the mass spectrum helps identify the compound or structure. An example has been shown before.

py-GC-MS

As already described, polymeric organic material can be vaporised by quick pyrolysis. For analysis of different oriental lacquer samples — however not from the Lintong Terracotta Army — two-step pyrolysis was used prior to GC-MS by Miyakoshi and co-workers. By this means not only the botanical sources of the lacquers could be distinguished, but the polymerisation and cross-linking mechanisms of the lacquer hardening could also be elucidated.

Acknowledgements

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Notes

4 See acknowledgements.

8 Analyses carried out by Hans-Georg Richter, Institute for Wood Biology, University of Hamburg, 1995.
10 The investigations were carried out by Herbert Juling at the Official Materials Testing Laboratory (MPA) Bremen, Germany (report no. MPA 3011/97, 1997). Experimental: mounting of samples (c. 5 mm diameter) on a gripping holder, shock freezing in melting nitrogen (-210 °C), locking in a preparation chamber and breaking perpendicular to the layer. Conductive sputtering with carbon, field-emission SEM, 20 keV, working temperature -130 °C. The pictures were taken in backscattered electron (BSE) mode.


13 Measurements by Angelika Sebalv at the Bayerisches Geo-Institut, University of Bayreuth, Germany. Experimental: Bruker MSL 200 (200 MHz), 4 mm zirconia-ceramic sample container holding 100 mg powdered sample; $\gamma_{10}$ = 8070 Hz; TC/2-pulse = 3 ms, contact time = 3 ms, recycle delay 3 s, dipolar dephasing delay 40 ms, recording period approx. 24 h.


16 Discussion of the method and detailed results are presented at this conference by Ingo Rogner.


21 Analyses carried out by Irene Fiedler, Doerner-Institute, Bayerische Staatsgemäldesammlungen, Munich (1995). Experimental: From each sample an aqueous extract was prepared (3 days/or 40 °C) in order to dissolve water soluble components such as animal glue. The insoluble parts then had to undergo a cleaning step in order to separate pigments and organic components. Hydrolysis of desiccated extracts and solid residues separately (HCI 6 mol/l, 110 °C, Reacti-Thern, Pierce); dissolution of amino acid mixture with acidic buffer solution and separation in the amino acid analyzer LC5000, Bioronik. The method is described in: Fiedler, I./Walch, K. in: Walch, K./Keller, J. (eds.): Lacke des Backe und Rokoko – Baroque and Rococo Lacquers (Arbeitshefte des Bayerischen Landesamtes für Denkmalpflege vol. 81), München (Lipp) 1997, pp. 297-204.


25 The analyses were carried out by Marina Van Bos, Institut Royal du Patrimoine Artistique (IRPA), Brussels (1995).

26 The measurements were carried out by Gerhard Heck at the Rathgen-Forschungsinstitut Berlin (1995, 1997). Experimental: Curie-point-pyrolyser (Horizon Instruments) at 610 °C, 1.5 s, sample amount m < 1 mg. GC: Hewlett-Packard HP 5890 Ser. II, Split mode 1: 8; capillary column HP 5 (50 m x 0.32 mm x 1.05 μm); carrier gas: He (0.5), 1.6 ml/min; entrance pressure 63 kPa; transfer pressure 85 kPa; temperature program: 0-1 min: 50 °C; 1-32.25 min: 8 °C/min heating; 32.25-40 min: 30°C; detector: FID (300 °C).


30 Analysis carried out by Christian-Heinrich Fischer, Hahn-Meitner-Institut, Berlin (1997). Experimental: Extraction of the solid sample with concentrated sulphuric acid (1 drop), followed by acetonitrile (60 μl) and water (40 μl). Separation of the centrifuged solution on a Eurospher C8-column (5 μm, 250x4 mm) connected with a Merck-Hitachi gradient pump (L.2000) and coupled to a diode array detector (Waters 990). Eluent: acetonitrile/H2SO4 (0.5 mmol/l), gradient of acetonitril from 10-30 % / 10 min, flow rate 1.5 ml/min.

有机考古计量学的分析方法及其在研究兵马俑中的应用

简介

自从19世纪50年代以来，一门用来研究过去的学科被称之为：考古计量学。它的主要任务是：探讨，材料分析和数据处理。科学的结论是建立在与考古学，艺术历史及保护科学相互紧密联系，并共地进行讨论的基础之上的。这个报告的主要意图是想在有机考古计量学的方法上给出一个全面的观察和研究综述。从这个意义上讲，有机考古计量学意味着一种科学方法的应用，对于在考古对象及挖掘现场中的有机物的鉴定。这些物质大多数是来自于原始的天然产物，如：油、脂肪、蜡、亚麻材料，碳水化合物及纤维素、蛋白质、天然树脂和染料。

化学分析显示出这些材料的物理构造，多数情况下甚至可以用来辨别并保护考古对象和艺术品。经典化学分析方法所要提供的数据是很有必要的。然而另一方面，分析结果的准确度一般来说是很低。利用红外光谱只能对物质在种类上加以区分。出于实用的原则，可将有机化学仪器分析手段分成光谱鉴定和物质的色谱分离两部分。图1展示了两种极为重要的分析手段，并对它们在研究考古学中的应用进行了简要的概述。

在大多数有机分析方法中，通常需要隔离样品。但在研究极有价值的考古对象和艺术品的时候，这往往是一个严重的缺点。尽管如此，现今的许多分析方法所需要的是样品量，少到只有纳米克级（ng）。这样少量的样品量，是我们很难用肉眼看到的。这样一来，取样技术就成了分析过程中最重要的一步，这直接关系到研究对象的维护问题。

在这里进行讨论的一些方法，是在许多科研同仁合作研究中研究的最主要的hack部分所应用到的。这里给出的理论是结合发现的结论。这项研究的重点集中在复杂性的基础上。由于这一过程的变化极其敏感，所以它对复杂性的保护起着决定的作用。一些在这个联合研究项目中所作出的科学结论已经被更为详细地发表在其它一些地方。

显微镜检测法

光学显微镜检测法

尽管光学显微镜检测法几乎是在艺术和考古的研究工作中最早使用的技术工具，然而迄今为止，它的应用性仍显得十分有限。光学显微镜检测法的放大倍数可达1500倍。在利用大量的各种各样的技术装备及特定的光学效应的情况下，无论是穿透射线技术还是表面射线技术的应用都是在

纤维和木制品的鉴别

偏振光显微镜检测发，是一个众所周知的穿透射线法，适用于光的表面。此外，纤维在偏振光下也显示出特定的光学效应，这种特性可以用来鉴别天然的动植物纤维。如图3所示的切片样品之后，可使用穿透射线光学显微镜检测法来对它们进行植物学的鉴定。

应用

兵马俑被放置在地下的木制结构中。其中大部分的木器至今已腐烂或炭化。鉴定这些木器所用的种类便成为考古研究中的一大兴趣点。如图2所示的木制和蜡的样品，我们进行了植物学的鉴别，图2。令人惊奇的是，炭化的样品显示出不同的木类种类。很明显，在当时的建造工作，木材的来源并没有得到很多的重视。

地层学

来自木制品的表面的样品一般被进行横截面的制片。为了研究它们层的结构，通常将打光的横截面在表面光显微镜下进行研究。一些物质层在紫外线下由于它的荧光特性而发亮。

应用

兵马俑所使用彩绘的涂层，是通过表面光显微镜检测法进行检测的。在可见光下，兵马俑表面层的特征看上去不是很明显。但在紫外线下，这层漆显示出现微弱的黄色光荧光。从这里可以辨别出厚度为0.1mm的两个涂层(图3)。另一个孔是紫外线下可以看到在完全干燥的层有許多洞和毛细孔。此外，其它被检测的层样品却拥有较密的结构。

扫描电子显微镜检测法

概述

扫描电子显微镜检测法(TEM)是一个用以观察细微样品的有
力工具。在艺术和考古研究领域中，它的放大倍数通常可达达到一万倍。在无机材料，包括元素分析的领域中SEM具有特殊的一部分。这项技术还具有高分辨率和高放大倍数的优点。然而普通的SEM要求使用完全干燥的样品；使用cryo-SEM（低温扫描电子显微检测法）能够看到潮湿样品的结构，甚至于水本身。Cryo的意思是指，无论是样品的准备过程，还是显微观察过程，都是在极低的温度下进行的。在将潮湿的样品送入显微镜之前，先将其在液氮(-210°C)中骤然冷却。在此过程中，样品所含水的成分处于固体的无定形态状。这样一来，就使得样品的潮湿结构得到了保护。

应用

使用cryo-SEM对兵马俑的原始边缘进行了研究，用以展示其潮湿的微观结构相对于其干燥的微观结构。图4展示了潮湿状态下的双底色层。在这里，可以清楚地看到两个涂层，它们显示出一个紧密的结构和典型的细长的形状。在高倍显微镜下，可看到它的直径低于0.1 μm。

将真空室的冷却切割后，样品在高真空状态干燥。这个操作过程中其中一个涂层的彻底烘烤（图5）。底色在干燥过程中的卷曲或许能够解释这一现象，尽管这一过程要明显地在图上进行很激烈。在生存的那一流层上形成了一些直径大于10 μm的孔洞，这一层的出现和被空气干燥的涂层结构（见图3）紧密相关。

光谱检测法

简述

光谱检测法通常是在使用电磁波辐射与分析物的相互作用的原理上。电磁波的辐射强度在经过吸收，反射，及反射过程之后会被衰减。在电磁波谱中，不同的波长范围被应用于各种不同的分析手段：高能量的X-射线在不适合用于有机分析，但对于使用X射线荧光法（XRF）和X-光片进行的元素分析还是很有用途的。用于样本染色可选择紫外-可见光-光谱法（UV/Vis）。红外光谱法（IR）使用的辐射能量低于可见光，它不仅可以用来分析无机物，也可以分析有机物质。核磁共振法（NMR，简称：核磁）所使用的波长在无线电波范围内。在这种情况下要使用外加磁场，从而广泛的意上讲，不同的粒子，可根据它们质量的中性加以区分。这种因质量不同而引起的粒子分布也同样可以由光谱学的角度进行处理。这就是质谱法（MS）的原理。

红外光谱法

概述

红外光谱法是建立在分子中化学键对红外线吸收的原理上。在红外光谱中，吸收和透射光强度被作为辐射能量变化的函数，辐射能量由波数给出，单位是cm⁻¹。红外光谱法适用的范围很广，它可用来获得纯物质的准确的分子结构信息；对于混合物可使用官能团的特征表现来进行区分。尽管如此，在通常情况下这种方法却无法用来更精确地判断脂质，油，或者蛋白质。红外光谱法在工业中可以鉴别人工合成的聚合物。通常情况下，将测量的谱图与已知物质的参照谱图进行比较。

现今主要被使用的是经过傅里叶变换的红外光谱法（FT-IR）。傅里叶变换的红外光谱法使得显微镜检测法和红外光谱法的结合成为可能。这项技术只需要直率为30微米，或质量为30微克的样品量。通常与这项技术一同使用的是一个叫做钻石镜片的配器。傅里叶变换红外光谱-显微镜检测法的优点在于：样品用量少，数据处理迅速，应用范围广。由于这项技术不损坏物质结构，所以分析过的样品可以用来作为进一步的分析使用。

拉曼光谱法是最近红外光谱法中的一种分析手段。在这里，分析物在照射下所发射的散射光被进行捕捉和记录。由此而获得的样品谱图可在红外波长范围内。由于所记录的是散射光，所以这项技术不需要使用被隔离的样品。事实上，拉曼光谱法是迄今为止唯一的一种来获取物质的有机化学信息而不进行任何结构损伤的分析方法。然而，拉曼效应非常微弱，所以在拉曼光谱法成为艺术和考古研究工作中的常规方法之前，还有很多设备技术上的问题有待解决。

应用

在处理兵马俑的具体问题上，微观化学实验反应在鉴定原层底色上取得了成功。首先由FT-IR证明：墓葬部分是来自东汉的“生漆”，将从一个样本样品上断裂下来的两个碎片进行FT-IR的测试，这两个碎片的FT-IR谱图看上去没什么相互间具有高度的相似性，而且和参照样品谱图也极为相似（图6）。在研究和不同的粘合介质相混和的人工合成漆的时候，发现，对于添加物的鉴定是很难用FT-IR-光谱法来实现的。

NMR

核磁共振谱检测法（NMR）的原理是建立在，当某种特定的原子核暴露在磁场中时对电磁波辐射所产生的反应上。最重要的“核”应数：氢（H，质子）和碳（C）。每个不同类型的原子及官能团都会产生不同的特征信号。这种特征信号用“化学位移”δ（delta）的方式表示，其单位为ppm。此外，从NMR-谱图上可获取“定量”的信息。

质子和13C的核磁检测法主要适用于对有机分子结构的鉴定。在考古及维护领域中，核磁检测法曾经成功的应用在鉴定树脂，琥珀，焦油，蜡和硬柏脂。此外，这种方法也被广泛地应用于检测水或加固剂在考古对象中的分布。核磁检测法的优点在于：测量及数据获取可同时进
行，高分辨率(区分官能团)，但在另一方面，在研究混合物是无明显的，其分辨率却很低。以前的质谱仪可以分析液体样品。这个缺点如今已被特殊的测量技术所克服：交叉极化和静电自旋的固态13C-NMR(13C CP/MAS)。与1H-NMR相比，13C-NMR的灵敏度要低很多。这就需要较短的测量时间和相对较大的样品量：50至250 mg。而且，样品需要事先被粉末化。在考古学应用中出现的问题是：核磁的测量会受到顺磁的杂质如铁盐的强烈的干扰。

应用

对来自兵马俑底部的样品及人工模拟的样品进行了固定相-碳13-核磁共振的检测。两个样品谱图的基本形状十分相似(图7)。这就证明了，兵马俑底部的组成部分来自东方所的假设。这些样品的成分之一在于含有官能团的含量(带氧的芳香碳原子的化学学位移通常在145 ppm)。而羰基官能团的化学学位移是175至200 ppm)，这是由于原始样品的氧化层所引起的。

质谱检测法(MS)

通常情况下，在质谱仪中的分析物被转化成带电荷的粒子。这些带电粒子在电场中得到加速，并能根据它们本身的不同质量和所带电荷数被分离开。在因此而得到的谱图上，显示出这些具有一定质量比的粒子的相对丰度。质谱技术种类繁多，显示这些技术及其在有机考古计量学中的应用在这里是不可能做到的。常见的有气相色谱与四极质谱结合。

“直接温度解析质谱”(DTMS)中的样品被加热气化。这种方法在过去曾被用来进行精制催化剂的分析。和高分辨解析谱后的样品进行渐进缓慢的升温至最终温度，这样，便可在含有热聚合物或样品中低分子量的化合物。DTMS的优点在于：样品需量少，分析时间短，样品不需要进行预处理。

“载荷支持的激光解析离子化”(MALDI)是在质谱法中一个非常重要的气化-离子化的技术。这种方法在对高分子量，低挥发性的物质，如生物大分子，的分析中具有特殊优点。在一些分析样品，包括兵器俑底部的分析中曾使用了MALDI-MS。

色谱法

简介

色谱法是一系列用于物质的分离，鉴定和定量的分析技术。这项技术的基本原理是：物质的迁移，这种迁移是建立在物质在不相容的两相中的不同分布的基础上的。混合物在分层系统中的分离决定于该混合物的组分在这两相中的分配情况。在这两相中的一相是：固定相；另外的一是流动相。根据固定相的安装可区分平面层析法和柱层析法。早期的平面层析法使用的是上片，以后出现了涂有玻璃覆盖层的。目前，用于分析目标进行应用的大多数平面层析法(TLC)是使用涂有乙烯基的硅镜所涂盖的塑料片或铝片。平面层析的在艺术和考古工作中的应用已有近50年的历史，特别是应用于染料，多糖，树脂及蛋白质。高效薄层层析法(HPTLC)的出现使得许多的分析手段更具生。这项技术的特征在于：由极细的微粒构成的非常薄的固定相。在平板层析法中，分析物停留在固定相上，并形成一个所谓的“内部层析”。每一个混合物中的组分都是由它们的相对移动相前峰行程距离(由Rf来表示)来进行区分的。

在正常情况下，柱层析技术实际上使用的是毛细管的种类，是根据固定相的固有特征而进行区分的。在液相色谱图，气相色谱(GC)以及超临界流液色谱(SFC)中有很多不同种类的技术得到发展。由柱层析技术所得到的“外部层析”。它的意思就是：分析物的检测是在柱上的流动的层析结果是由检测器所显示的信号作为时间的函数来表达的。它的特征值被称为“滞留时间”(T)。

在色谱技术中被分析的物质要进行移动。这就要求该物质要么在使用TLC和GC时可溶解，要么在使用GC时易挥发。天然的聚合产物(蛋白质，糖类，干燥的油类)必须使用化学手段进行降解至它们低分子量的结构单元 – 大多数是在水溶液中进行水解。

液相色谱

概论

液相色谱可用于分离不溶，极性和高分子量的物质。高效液相色谱(HPLC)的分析时间短，使用高压，细层析柱。早期的HPLC层析柱所使用的物质要溶剂更投合极性。现今最频繁使用的方法是：色谱-高效液相色谱。这里的固定相要层析柱更极性。在液相色谱学领域中，HPLC被用于分析来自于蛋白质的氨基酸，糖类及碳水化合物。

蛋白质可由其氨基酸的组成来进行鉴定。不同种类的氨基酸使用其特有的氨基酸来作为连接媒介。蛋白质在水解之后所产生的氨基酸混合物被通过液相色谱进行分离和鉴定。所使用的层析柱的填充物是离子交换树脂。许多年来，这种以“蛋白质分析”为形式的分析手段被应该用于解决艺术和考古学中所出现的问题。一种近来用以检测蛋白质的HPLC-分析方法曾在一篇文章中得到具体的描述。在这篇文章中使用了特殊的水解和纯化方法。

应用

使用离子交换液相色谱来分析兵马俑原始涂层的样品及两个对照涤的样品，其目的在干检测样品中可能含有的蛋白质。结果发现，无论是在原始样品还是对照样品中都不含有水溶性的蛋白质组分。从水不溶性的原始基底残片样品
中得到了氨基酸的结构，这与含有血猪的参考样晶极为近似。这个初步的结论暗示着，兵马俑的陶器晶体中曾被加人了猪血。在任何一个原始的样品中都没有检测到动物胶。尽管如此，还是应该对更多的原始样品及不同的参考材料进行分析，用以证实这个假设。和基层材料相反的是，两个被分色的涂层样品中含有一些低浓度的氨基酸。

简介

“双联法”一般是指两个或多个独立的分析技术手段的结合。因为紫外/可见光谱、红外光谱、质谱及核磁。多种强有力的后定分析技术就是一种这类的多维系统，它们通常都是与计算机连接用来处理大量的数据。

气相色谱

概论

气相色谱(GC)在近几十年来被用于分离具有挥发性和极性的混合物中的组分。在这项色谱技术中，是以气体作为流动相，其固定相是液体。在艺术和考古学领域中，气相色谱以被广泛应用用于有机材料的分析。

在气相色谱中，气相色谱技术中的样品被载气的推动下通过一个细又长的，被称为“柱色柱”的毛细管。柱色柱内部表面上要有固定相，这是一种具有固定点的液体。柱色柱在通常情况下被进行加热。在柱色柱的顶端，可将从样品中分离的组分用检测器进行检测。最常用的检测器的类型是：热解离子检测器(FID)，目前最常使用质谱仪作为气相色谱的检测器。

液相色谱，气相色谱的结论是谱图也是由时间曲线所表达的。

液相色谱-紫外/可见光谱法(HPLC-UV/Vis)

概论

液相色谱由于检测器的非高灵敏度，非选择性而受到阻碍。为了克服这个缺点，经常将液相色谱与光谱分析手段相结合。对于在考古及艺术领域中有机染色的检测，很显然是紫外/可见光谱(Vis/UV)光谱手段。在溶剂通过HPLC-毛细管之后，由一个对不同物质重复进行紫外/可见光谱检测的二极管阵列检测器(DAD)将其进行检测。结果一般是由液相色谱图给出。此外，对每一个滞留时间都有紫外/可见谱图的记录。因此在液相色谱图上的每一个峰值都可以通过其用来表达某一特定染料的特征谱图来进行辨认，这一分析手段的灵敏度可达到纳米级(nm)。

应用

在兵马俑的研究中，高效液相色谱-紫外/可见光谱法(HPLC-UV/Vis)被用来进行各类色中展示裸露皮肤的玫红色部分样品的分析。这种类型的检测设备可能含有有机染料，原因在于其出土后暴露在阳光下而促进颜色变化。然而，在研究中还没有报告过在玫红色层中发现有机染料。尽管如此，用这种对光敏感的玫红色染料来自于某种有机染料，不同意它是由无机色素硫化汞矿(朱砂)制成的。

气相色谱-质谱法(GC-MS)

概论

很多有价值的、用来分析低分子量有机物混合物的分析工具，都是气相色谱和质谱的在线组合(GC-MS)。在考古和艺术领域也是如此。大量的对来自艺术品的材料进行研究的工作已经得到发表，其中还包括树脂、油料、蜡和蛋白质等。

在这个系统中，气相色谱法作为分离技术，一个四极质谱仪是用于对各组分进行分子鉴定。GC-MS的一大优点是对混合物中极性物质进行检测的能力。这对考古和艺术研究工作是十分重要的。但另一方面，只有可挥发的物质能够被直接地进行分析。这就需要有时使用高灵敏度的技术手段对要分析的物质进行浓缩和预前处理。此外，结论中的质谱图通常是很复杂的。这由
于在离子化过程中被分析分子的断裂而造成的。
从GC-MS装置而得出的二位数据可推得如下的图谱：
1. 总离子流色谱图：对每一个滞留时间都将信号进行叠加。在这儿，质谱只是作为一个检测器，类似于传统的柱层析方法。
2. 质量色谱图：在这一，质荷比信号强度是在建立在滞留时间的基础上绘制的。借此，可将某一特定化合物产生的离子特征从色谱图上分离出来。
3. 质谱图：对于给定的滞留时间，质谱可以帮助鉴别化合物及其结构。前面已经介绍了一个这样的例子。

热解气相色谱-质谱法(HP-GC-MS)

正如所描述，聚合有机材料可通过热解的办法进行气化蒸发。Miyakoshi和他的同事们在对不同的原始样品（并非来自临潼兵马俑）进行分析时，曾在GC-MS之前使用了两步热解法。使用这种手段，不只可以对来自于植物的漆进行研究，而且硬化漆的聚合及交联机理也可得到阐明。

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注：
尾注请见英文文本。
New Methods to Characterise and to Consolidate the Polychrome Qi-lacquer of the Terracotta Army

Abstract

A method for the conservation of aged qi-lacquer layers on silicate material such as terracotta is described. Detachment of the layers would result in the loss of the paint layer. The terracotta army of the Chinese emperor Qin Shihuangdi in Lintong / China is a prominent example of this problem because the paint layer is bound to the surface by an intermediate qi-lacquer layer. This layer has aged 2200 years, buried in wet clay and will detach from the surface if relative humidity drops below 84 % after the excavation. Methacrylic monomers were of special interest as solidifying materials because of their long lifetime and their excellent transparency. Lacquer samples were treated with watersoluble 2-hydroxyethyl-methacrylate (HEMA) which was polymerised by electron-beam radiation with an electron energy of 1.0 MeV. In the experiments the dose was administered in three steps of 20 kGy. Micro-organisms and mould are destroyed by the electron-beam radiation. Infra-red and mass spectroscopical evaluation shows no damaging effect of electron-beam radiation (300 kGy) on the qi-lacquer. Original qi-lacquer and lacquer consolidated with the method described above were characterised by laser desorption mass spectroscopy (LD-MS). The formation of HEMA polymers with 4-6 monomer units within the lacquer was proved by laser desorption MS. Infrared spectroscopy reveals that the degree of polymerisation is proportional to the applied dose.

Three original polychrome fragments were successfully treated by electron beam curing. The qi-lacquer is bound to the terracotta, the fragments can be dried, a natural look (not shiny) of the polychrome surface is obtained. Laser video holography was employed to investigate if drastic changes in humidity will affect the consolidated polychrome layer. No damage could be detected after four humidity cycles (35-83 % r. h.). The long term stability will have to be evaluated.

The application of electron-beam polymerisation seems to be a promising method for the conservation of the terracotta army of Qin Shihuangdi and other works of art.

Introduction

The change of polymeric bindings with time is an important factor for the ageing of art objects. The detachment of qi-lacquer layers (urushi) from the basic material would result in the loss of paint layers and solidifying such layers is a central point in the conservation of such works of art. The terracotta army of the Chinese emperor Qin Shihuangdi in Lintong / China is one of the most important archaeological objects and is a prominent example of this example because the paint layer is bound to the terracotta surface by an intermediate qi-lacquer layer. This layer has changed during the long time span of 2200 years, buried in wet clay so that it detaches from the surface if relative humidity drops below 84 %. This condition occurs during excavation of the coloured fragments. Until now, the conservation of the paint layers is an unsolved problem.

Results and Discussion

We tried to rebind the qi-lacquer layer to the terracotta by the application of organic polymers. This seems to be an extraordinarily difficult problem if the support is not an organic material, but a highly hydrophilic surface of a silicate such as terracotta. The application of radical initiators and monomers such as methacrylic esters solidified the qi-lacquer, but could not bring about a firm connection of the lacquer to the terracotta support. Inorganic pigments constitute the polychromy of the conserved works of art. A second problem was the lustrous surface of the solidified material which impairs the visual impression by changing the tonality of the colours.

We wanted to avoid these problems by the application of a two-step process. Firstly the terracotta and the overlying layers were impregnated with cotton wool compresses containing the liquid monomer. The monomer concentration in water was increased to 100 % in several steps. During this process unwanted polymerisation was inhibited by the stabilisers which are generally added to the monomers to allow storage (up to 650 ppm hydroquinone-nomethylthylene). Thus the monomer had enough time to penetrate all organic and inorganic material.

Secondly the polymerisation was induced. This could be done neither by conventional thermal radical initiators nor by photo-polymerisation which was prevented by the dark colour of the lacquer layer. Therefore we tried initiation by penetrating radiation with which we could start polymerisation from within the terracotta support.

Polymerisation by the application of X-rays gave very poor results. The photons were not absorbed properly within the thin qi-lacquer layer and the silicate material to induce polymer formation.

However, good results were obtained by the application of an electron beam for initiation. This forced the start of the polymerisation within the terracotta propagating toward the outside through the monomer impregnated qi-lacquer to the outside air. After the electron radiation is switched off, there is no radioactivity left within the irradiated material; of course there is a very intense X-ray radiation during the application of the electron beam which must be thoroughly shielded. Methacrylic monomers were of special interest as solidifying materials because of the long lifetime and excellent transparency of their respective polymers. Methylmethacrylate seemed to be less suitable because of its low polarity so that watersoluble 2-hydroxyethyl-methacrylate (HEMA) gave even better results. It was applied as a commercial formulation Plex 6803-1 (Rohm). Detachment of consolidated qi-lacquer by volume shrinking of HEMA cannot occur because of the thin HEMA layer.
Polymerised HEMA can take up water up to 40% of its own mass. This implies that the polymerised product lets water penetrate. If applied to wet terracotta water can cross the polymerised HEMA film and evaporate. In contrast to a film which seals the surface, the formation of blisters can be avoided.

The application of an electron beam (EB) initiates a radical polymerisation which is inhibited by molecular oxygen contained in air. Therefore oxygen must usually be thoroughly excluded to obtain a smooth and solid surface. On the other hand, the influence of oxygen is desirable for obtaining a lustreless surface of the solidified works of art. Therefore one should initiate the polymerisation with electron beam radiation with air surrounding the monomer soaked qı-lacquer layer. After the EB cure small residues of monomer can easily be removed from the surface by wiping off or by evaporation of the monomer at room temperature.

A central difficulty in conserving paint layers by the application of electron beam polymerisation is the potential damage of the lacquer by radiation. Ions and radicals remaining after the radiation process can be starting points for further decay. The qı-lacquer, however, contains ortho-hydroxy phenyl moieties which are known to be radical scavengers.

Electron beam curing experiments were carried out at the Institut für Polymerforschung (IPF) in Dresden with the Russian electron accelerator ELV-2, INP Novosibirsk. A sketch of the electron accelerator is shown in Fig. 1. Electron energies can be varied between 0.6 to 1.5 MeV, the maximum radiation current amounts to 25 mA. For further experiments in Xian the electron accelerator ELV-8 can be used. This apparatus is from the same Russian producer and provides a wider range of electron energies.

The electron beam (EB) is focused and scans the substrate. Extensive shielding is required due to "bremstrahlung". The absorbed dose the sample receives as a result of passing under the beam is obtained by integration of the Gaussian function for the beam shape. The sample speed is thus inversely proportional to the absorbed dose. In the experiment the dose was administered in steps of 10 and 100 kGy. The total dose absorbed is the sum of all the individual doses.

For all experiments an electron energy of 1 MeV was used. This value determines how deep the radiation can penetrate into a substrate. At an energy of 1 MeV electrons can penetrate up to 5 mm into a medium of density 1 (water), with a maximum intensity at 1.6 mm. At longer EB exposures if all monomers are consumed by the polymerisation reaction main chain scission is possible.

### Preliminary Experiments

In preliminary experiments original qı-lacquer ground layer flakes were flattened on a terracotta support with H2O dest. and were impregnated during three days with various consolidants before electron beam irradiation.

The HEMA formulations polymerised at an energy dose of 50 to 60 kGy. Polymerised Plex 6803-1 shows the best results concerning the mechanical strength of the binding of the qı-lacquer. Unreacted monomers on the surface evaporated after a few days. After three years the original Qin-dynasty qı-lacquer is still firmly bound to the terracotta, the surface is not shiny or lustrous and the terracotta has completely dried.

![Fig. 1. Sketch of the electron accelerator ELV-2, INP Novosibirsk.](image)

图 1. ELV-2, INP Novosibirsk 电子加速器示意图。

### Analytical Methods

Among the methods that we have used, I want to focus shortly on the following three:

**Infra-red spectroscopy**, cross sections / microscopical evaluation and laser desorption mass spectroscopy.

### Infra-red Spectroscopy

Infra-red Spectroscopy does not show damaging effects of the electron radiation up to 300 kGy. Spectra taken from irradiated and not irradiated samples were alike. No damage by electron beam irradiation can be detected by infra-red spectroscopy.

### Infra-red Investigation of the Degree of Polymerisation of Pure Monomer

In order to find the best conditions to consolidate the monomer soaked samples a multitude of preliminary experiments were carried out. Test tubes were filled with equal amounts of the respective consolidant. Some of the test tubes were filled with the inert gas argon to exclude oxygen which is known to be a radical scavenger and polymerisation inhibitor. The test tubes were exposed one or more times to a certain dose of electron beam radiation to evaluate differences in the effect of the irradiation.
The effect of argon to exclude air (which contains oxygen and thus inhibits polymerisation) is only minimal. If Plex 6803-1 is irradiated in argon atmosphere the dose necessary for consolidation is only lowered by 10 kGy down to 50 kGy. The exclusion of oxygen can lead to the formation of a transparent and shining film on the surface of the consolidated original qI-lacquer. The use of argon “blanketing” is thus not recommended.

Pure HEMA cannot be polymerised as easily as the HEMA formula Plex 6803-1, which contains a few percent of cross-linker. Plex 6803-1 is therefore found to be superior to pure HEMA.

The dose necessary to obtain the solidification of Plex 6803-1 was found to be 60 kGy. In different experiments the dose was administered in one step, in two steps (20 kGy + 40 kGy) and in three steps (3 x 20 kGy). All experiments proved the Plex 6803-1 to be solid after the irradiation. It can thus be confirmed that the overall dose given is of importance, independent of the number of steps it is accumulated in.

During all experiments the accelerating voltage is kept constant at 1 MV. In the last set of experiments the radiation current of the electron beam was varied. The lower the radiation current the less electrons penetrate the monomer soaked samples. The lower the amount of electrons initiating a polymer chain, the longer the polymer chains grows. This means that longer polymers form at a lower radiation current. At 2.4 mA a dose of 60 kGy resulted in solidification and evaporation of monomer. Too much energy is transferred in this one step treatment. At the lowest radiation current of 0.6 mA the maximum dose obtainable in a single step is 25 kGy. This treatment led to the formation of a very hard solid.

The solidified samples of Plex 6803-1 were further investigated by quantitative infrared spectroscopy with a Perkin-Elmer IR-1420 FT-IR spectrometer. This method allows to determine the degree of polymerisation. The samples investigated had very different consistencies: liquid, viscous, rubber like and rock hard. It was preferred to monitor a peak that was linearly proportional to the degree of polymerisation. The polymerisation of Plex 6803-1 afforded the formation of linear chains like: 

\[-\text{CH}_2\text{-CR}_{2}\text{-CH}_2\text{-CR}_3\text{-}\]

The newly formed methylene group \((\text{CH}_2)\) is found at 748.5 cm\(^{-1}\) and its peak is proportional to the degree of polymerisation. The longer the chain the more methylene groups are formed, the higher the absorbance at this wavenumber.

After thorough investigation the IR-spectra were normalised for the \(-\text{CH}_2\text{-H} \) valence vibration at 2957 cm\(^{-1}\) (methyl group is not affected in the reaction). The baseline was corrected and the wavenumber 780 cm\(^{-1}\) was set to zero. Fig. 2 presents IR spectra focusing on the peak at 748.5 cm\(^{-1}\) taken after a single step electron beam curing with doses from 0 to 80 kGy. The proportional relationship between dose rate and absorbance is evident.

At a dose of 80 kGy the Plex 6803-1 became solid, independent of the number of steps. The single step electron beam treatment leads to a higher degree of polymerisation. Fragment F009-98 was consolidated with a dose of 4 x 20 kGy.

The lowest dose necessary to obtain solid Plex 6803-1 was found to be 60 kGy. The dose was applied in a single step, in two steps (20 kGy + 40 kGy) and in three steps (3 x 20 kGy). The resulting spectra are shown in fig. 3. All three curing methods afford about the same degree of polymerisation. This dose was to be used for one of the original polychrome fragments (Fragment F011-98).

In another set of experiments the electron beam current was varied. The lower the beam current, the longer the polymer chains, the higher the absorbance at the \(\text{CH}_2\) rocking vibration (748.5 cm\(^{-1}\)). Fig. 4, shows the spectra taken from samples irradiated with an electron beam with a beam current of 0.6, 2.4 and 4.2 mA.

The highest degree of polymerisation was obtained at 0.6 mA. The solidified Plex 6803-1 was rock hard. The original fragment F006-98 was treated in this way. Irradiation with a beam current of 2.4 mA (60 kGy) resulted in the evaporation of the consolidant. Although longer polymers are formed the detrimental effect of the heat-up of the polychrome lacquer and the fragment disqualifies this curing method for further experiments.

Although FT-IR Spectra allow for a quantitative measurement of the relative polymer length, further experiments will have to be done to determine the distribution of the absolute length of
the polymer chains after electron beam curing. Laser desorption mass spectroscopy (LD-MS) is an elegant method to obtain the exact mass distribution.

Cross Sections and Microscopical Evaluation

Light microscopical investigation and cross sections provide another possibility to evaluate the penetration of the consolidant into the lacquer and the terracotta. Original qi-lacquer samples consolidated with electron beam and the HEMA formulation Plex 6803-1 were used. At magnifications of 50 x to 200 x a colourless transparent polymer film of Plex 6803-1 can be detected between terracotta and qi-lacquer. This can be clearly seen in the cross section. However, on top of the qi-lacquer no polymer film is found. Owing to this the surface of the consolidated qi-lacquer appears dull, it does not shine.

In this cross section the polymerised HEMA layer is thicker than the original qi-lacquer layer. This is due to the fact that detached original flakes were consolidated onto a new terracotta support. Original samples, where the lacquer layer still adheres to the original terracotta, do not show an intermediate HEMA layer after consolidation.

Laser Desorption Mass-spectroscopy

Laser desorption mass spectroscopy (LDMS) was carried out on irradiated samples at the Max-Bern-Institute in Berlin, Adlershof, Germany. The degree of polymerisation of the applied monomer and possible EB cure damaging effects were monitored. For laser desorption a XeCl excimer laser LPX-100 Lambda Physik (308 nm, 30 ns pulse width) was used. The positively charged ions generated were separated by a non-commercial reflectron time-of-flight mass-spectrometer (RETOF-MS, see fig. 5.) with a mass resolution\(^1\) of \(m/\Delta m = 2000\). In contrast to most commercial systems, the laser desorbed ions were allowed to drift for ca. 2 cm before being extracted by a pulsed electric field. The ions were detected by dual multi-channel plates and the signal was collected by a digital oscilloscope. The spectra were then transferred to a PC for further evaluation. The delay between laser pulse and ion extraction allows one to preselect the mass of the ions detected.

Mass-spectroscopic evaluation shows no damaging effect of the EB radiation (300 KeV) on the qi-lacquer. To prove the polymerisation of the applied monomers within the terracotta and the original qi-lacquer LDMS spectra were taken. LDMS of HEMA polymerised by electron beam curing usually determines the average polymer chain length in the terracotta support and within the qi-lacquer. The spectra are depicted in fig 6.

In the terracotta support only polymer fragments mainly consisting of 2-4 monomer units were detected. Within the solidified original qi-lacquer layer solely fragments with 4-6 monomer units were found. Unfortunately the LDMS spectra do not show...
long polymer chains, but only fragments of these. The reason for this is the three-dimensional cross-linking, which occurs during the polymerisation. A large network is formed and the laser pulse can only desorb small parts of this network. For every polymer a combination of peaks can be observed. This is due to sodium and lithium adduct peaks and because of the cleavage or addition of a hydroxyethyl fragment (small bond dissociation value). In the mass spectrum of HEMA polymerised in terracotta fewer lithium adduct peaks can be found. Furthermore hydroxyl endgroups are detected which were formed through EB radiation by reaction with the terracotta.

Investigation of the influence of electron radiation on qi-lacquer by IR and mass spectroscopy confirmed that even a dose of 300 kGy (30 Mrad) does not result in a detectable damage of the qi-lacquer. However this dose is far beyond the dose which is necessary for polymerisation. Additionally the radiobiological effect of electron beam and "bremsstrahlung" destroys micro-organisms and can be used to disinfect contaminated lacquer.

After the promising preliminary experiments we started experiments with original samples. The experiments were performed at the Institute for Polymer Research in Dresden, Germany by the Bavarian State Conservation Center and three Chinese colleagues from the Museum of the Terracotta Warriors and Horses: Zhou Tie, Rong Bo and Zhang Zhijun.

Before the irradiation with the electron beam three original samples (Fragment 6-98, 9-98 and 11-98) were pre-treated as follows: During three days the samples were impregnated with the commercial formulation Plex 6803-1 which was applied with compresses. The concentration of Plex 6803-1 in water was raised from 33% on the first to 66% on the second and finally to 100% on the third day. Thus the consolidant had enough time to penetrate the qi-lacquer, its overlying paint layer and the terracotta. In order to evaluate different electron beam curing methods every original fragment was treated with a different method.

**Fragment F006-98**
Part of body armour with qi-lacquer and red iron oxide. Treatment: 1 time 25 kGy at 1 MeV and 0.6 mA.
The fragment was not cleaned after the irradiation. Surplus consolidant was allowed to evaporate for several days. After irradiation the sample was stored under ambient conditions.

**Fragment F011-98**
Part of body armour with qi-lacquer and stripes of red cinnabar. Treatment: 3 times 20 kGy at 1 MeV and 4.2 mA.
The fragment was not cleaned after the irradiation. Surplus consolidant was allowed to evaporate for several days. After irradiation the sample was stored under ambient conditions.

**Fragment F009-98**
Collar with Han blue, cinnabar, pink colour and qi-lacquer. Treatment: 4 times 20 kGy at 1 MeV and 4.2 mA.
Surplus consolidant was removed between the irradiation experiments with a laboratory tissue. Along rims and creases liquid consolidant collected to form a pool which can harden and lead to shiny spots on the treated fragment. These pools were drained by pressing the edges of the tissue into the rims and creases. The fragment was immediately freed from surplus consolidant after the last irradiation by pressing the laboratory tissue onto the lacquer. The result was a fragment with virtually no shining spots on the surface. The sample was stored under ambient conditions.

After irradiation all fragments showed a good mechanical fixation of the original qi-lacquer and the overlying polychrome layer. A rub test was performed. The terracotta dries out completely after a few days, the stability of the polychrome qi-lacquer is retained. All three fragments are in good condition after three years at ambient temperature and humidity. The coloured lacquer layers are bound tightly to their original terracotta support. A natural look (not shiny) of the polychrome surface is obtained. Laser video holography was employed to investigate if drastic changes in humidity will affect the consolidated polychrome layer. No damage could be detected after four humidity cycles (35-85 % r. h.). We are all looking forward to seeing the effect of long-time storage under ambient conditions in Lintong, China.

Finally I would like to repeat all advantages offered by the new method:
- The consolidant is watersoluble in every ratio.
- The consolidant is similar to water in viscosity, colour and density, it has only a faint odour.
- Only two solutions of consolidant in water are required for the whole preparation. No more chemical operations needed.
- The consolidant is a commercial formulation of HEMA (Plex 6803-1) which is commercially available.
- It is used in very hostile environment for long term sealing of broken canal pipes.
- The consolidant is stable under normal conditions, no auto-polymerisation occurs.
- Monomer treated samples can be stored because the polymerisation starts with the electron beam irradiation only.
- The polymer has an excellent transparency like most methacrylates, but treated samples do not have a shiny appearance.
- The polymer binds to qi-lacquer and terracotta alike.
- The polymer is not poisonous, it is the main component of contact lenses for the eye.
- Irradiation with an electron beam can be carried out in Xi’an, China with a suitable electron accelerator like the ELV-8. This apparatus was produced by the same company as the accelerator used in Dresden.
- Electron irradiation effectively destroys bacteria, micro-organisms and most important: mould.

The application of the rapid electron beam polymerisation is therefore a promising method for the conservation of the terracotta-army of Qin Shihuangdi and other art objects.
References


飘格纳

鉴定和加固兵马俑彩绘漆的新方法

摘要

本文介绍的是一种保护硅酸盐材料如陶俑上的老化漆层的方法。漆层的剥落会导致彩绘层的损失。这方面的著名例子是埃及文物兵马俑。因其表面彩绘层与一层漆中间层相连。这些漆层在湿土下埋藏了2200年，出土后一旦空气湿度降到84%以下，漆层便会与表面分离。作为固化材料，甲基丙烯酸单体值得特别重视。因为这种单体的寿命长，透明度好。漆样的处理，是通过约1.0 MeV的电子能量来聚合水溶性经乙基-异丁烯酸盐(HEMA)进行的。实验中分3步用20 kGy的剂量辐射。微生物和霉菌会被电子辐射杀死。红外线光谱和质谱分析显示，辐射(300 kGy)并不会对漆层造成损害。原始漆层和漆样用上述方法加固后，再经过激光解吸质谱(LD-MS)分析，激光解吸质谱证实漆中有4-6个单体单位的HEMA聚合物。红外线光谱显示，聚合度系与使用的量成比例的。

我们用电子辐射成功地处理了3块原始彩绘残片，漆与陶体附着，残片可以干燥。彩绘表面视觉效果正常(无发亮)。利用激光视频全息摄影，对剧烈的湿度变化是否影响加固后的彩绘漆层作了观察，经4组湿度变化(35-83%的相对湿度)没有发现任何破坏。长期稳定性还有待进一步评估。

用电子辐射聚合看来是一种大有前途的保护秦始兵马俑以及类似艺术品的方法。

(英译中：陈钢林)
Cristina Thieme

Paint Layers and Pigments on the Terracotta Army: A Comparison with Other Cultures of Antiquity

Today it is the terracotta itself – mostly gray, in parts reddish – that determines the chromatic impression made by the excavated clay warriors, but originally the terracotta figures were colourfully painted in rich contrasts. This polychromy was essential to the perception and appearance of the army. Research indicates that the extravagant polychromy of the clay figures is to be viewed as an imitation of the real appearance of the military uniforms of Qin Shi Huangdi’s army: “The colours of the clothes reflect the appearance of the Qin army and prove that in the Qin Dynasty the colours of the army uniforms did not mark differences of rank.” It is assumed that the Qin soldiers provided their own uniforms, having their clothes sewn from available materials. One soldier, for instance, wrote to his mother “[You should] look for low-priced silks or cottons which can be used to sew shirts and jackets.” The investigations undertaken so far give a fairly precise concept of the many colours and of the painting techniques used for the polychromy.

Figments with flesh-coloured pigments and/or remnants thereof make it clear that there is a great variation among flesh colours. Skin tones range from light to dark and from warm to cool pink; perhaps this was to more clearly characterize the imperial army, which was recruited from various peoples of different kingdoms. “In the 26th year of his reign (221 BC) Ch’in Shih-huang-ti annexed all the feudal lands under the heavens, brought peace to the people and declared himself the sole sovereign.” As a broken piece documents, the fingernails are done in white on top of the flesh colour. The pupils were left blank within an otherwise white eyeball, so that the dark brown lacquer of the ground remains visible. The hair likewise is the brown colour of the lacquer ground, being untreated with further colour.

Individual pieces of clothing are set in contrasting colours, for example a red top with blue pants. According to findings so far, the dominant colours for the costumes are red, green, blue and purple, more seldom yellow and white. So far no black has been found. Details such as collars or the hems of sleeves are set off in other colours. The uniform belts and the borders of the armor are mostly decorated with finely drawn and painted geometrical patterns. Chinese archaeologists have drawn up a detailed reconstruction of these patterns (colour plate IV, fig. 5-7).

The argument that the clay warriors wear over their clothes depicts leather armor made up of many plates, which frequently are held together by small green or red ties. At stomach and shoulder level additional red fabric ribbons join the plates together, allowing the armoured body to move more easily. The armor plates are coated with brown lacquer to represent leather. Grave findings from the Zhan-Guo Dynasty (Age of the Warring States, 481-222 BC) substantiate that the kingdom’s soldiers used shields and armor of leather that had been impregnated with lacquer. Impregnation was necessary to harden and stabilize the leather. The plates of the armor on the Qin terracotta soldiers are also coated with lacquer for the sake of realistic depiction. The fact that lacquer, rather than a paint layer of brown pigment, was used to colour the armour plates supports the theory that the terracotta army is to be regarded as an imitation of the real Qin soldiers.

A certain tension between the three-dimensional forms and the polychromy of the clay figures can be detected on the following details: Where there is only a layer of lacquer (as the ground) – i.e., where no thick-layered application of pigment was planned – the terracotta was always very carefully and individually worked. For instance, the hair on the figures is precisely incised, the soles of the shoes and the plates of the armour are differentiated. The light reflexes of the extremely thin lacquer layer make it easy to discern the finely incised decoration in the clay. In contrast, the sculptural elements that are covered with polychromy lack this finely detailed treatment. The pigment layers are conspicuously thick. This indicates that there was a foresighted overall plan for the appearance of the clay army already at the time that the figures were modelled, and that this plan took the differentiations in the polychromy into consideration.

The army of the First Emperor is characterized by such details as the differentiated flesh tones, the hair and pupils glowing with lacquer in contrast to the matte skin, the colour contrasts on individual garments, the fineness of the incisions and of the handling of the terracotta surfaces, and the geometric border ornaments. The different optical effects from surfaces treated with lacquer or with pigment suggest the materiality of the substance – leather or textile – that was being imitated. All of these techniques made it possible to produce a colourful, ‘alive’ and realistic army, created for the eternal soul of the emperor in an underground world without light, never intended for the eyes of strangers.

Even if the terracotta army is an imitation of the real army, there is still the possibility that the pigments and polychrome materials could have further significance and meaning. It is particularly conspicuous that very expensive, precious, artificially-made pigments (cinnabar, malachite, azurite, opiment, bone white, Han purple and Han blue) are documented for the polychromy of the clay warriors. Thousands of figures are painted with high quality pigments, of which an enormous quantity was needed. Yellow or green earth colours, i.e., cheaper and less colour intensive natural products, have so far not been identified. Whether these costly pigments document the luxury of the emperor or emphasize the status of his army, which had a preeminent importance during his reign, is an open question. Material value and aesthetic standards supplement one another in the case of an imperial patron. Valuable and costly painting materials were also enjoyed by the Roman emperors, but were denounced by Pliny the Elder as a waste; The pigments “that belong to the floridit’, or ‘blooming’, luminous colours, preferred by the ostentatious patrons because of their splendid appearance and their extravagance, were therefore not included in the supply contracts but had to be paid for separately or acquired by the patron.” Vitruvius documents the emperor’s love of ‘luxury’ pigments “with expressly sharp rebuke of the degenerate
taste that places value only on the cost of the pigment and not on artistic execution."11

In contrast to the Chinese and Roman desire for expensive pigments — on the part of emperors separated by worlds — in ancient Greece the effects of different ochre tones, the colori austeri12 of the so-called four-colour painting, were crucial. "To bring the art of the brush (i.e. of painting in its narrower sense) to fruition it was necessary to employ the pigments in richer nuances ... In this period four-colour painting was a consciously practiced colouring that apparently was intended to represent traditional values." Even if four-colour painting is a technique for wall paintings and not for sculpture, a painted polychrome design is also documented on Greek sculptures, for example on small terracotta figures from the 5th century BC with their surviving paint. "In the depths of the folds of their garments the large robed female figures on the gable of the Parthenon exhibit abundant remnants of a black pigment that apparently was intended to strengthen the natural shadow in the depths of the folds as well as the overall play of light and shadow on the figures. The same technique is found on the clay figures. The clay figure of a woman shown in a dance step wears a coat whose folds are in part flatly modelled. Only very strong brush strokes in a brown-red ochre strengthen the relief of the robes." For a correct interpretation of the iconological meaning of the pigments one must moreover take into consideration that, in contrast to the mighty temples of the Greeks, the terracotta soldiers were not created for a 'magnificencia publica'. The army was intended as a 'luxuria privata' of the emperor, for his underground, eternal life.

Painting Technique, Polychrome Build Up and Painting Materials

The fragments show differences in the build up of the paint layers. The build up consists of a dark brown lacquer ground, either one or two layers deep, followed by pigmented layers. It is not known if the terracotta surface was impregnated with a material that can no longer be identified today, before the ground was applied. The possibility of an impregnation is suggested by the lack of adhesion and by the absence of any discoloration of the terracotta because of penetration by lacquer. The sap of the East Asian lacquer tree Toxicodendron verniciflum (Chinese: qi; Japanese: urushi) is in any case a component of the brown to dark-brown ground, the lowest identifiable layer on the terracotta surface.13 Investigative methods included infrared spectroscopy, micro-hydroylysis, microchemistry and the scanning electron microscope. The two-layered ground, about 0.1 mm thick, is very sensitive to changes in moisture and reacts to loss of moisture with extreme shrinkage in volume, visible in drastic shrinkage-induced craquelure and severe arching of the existing scales. It is this extreme reaction of the ground to the loss of moisture that makes such complex conservation work necessary to preserve the polychromy. Apparently additional organic elements were mixed with the lacquer used to cover the clay figures; these additives could eventually explain the peculiar, extreme tension of the ground layer. It is still not known if the clay figures were painted according to techniques typical of the time, or if these techniques were used only for this grave complex. Polychromy work with comparable characteristics and conservation problems is unknown in the literature. Nonetheless, it cannot be ruled out that similar polychromy has been lost in excavations. Cheng Te K'un describes bronze and clay findings from the Western Chou era that were coated with lacquer: "...the decorative lacquer surfaces had flaked off... sometimes traces of the original lacquer surface may be seen." Mâchen-Helfen mentions a white drawing on a frieze with a lacquer ground in a grave chamber in Lo-yang from the pre-Han era; it could be rubbed off easily.17 The build up of the paint layers on small figures dating from the Han era, found at the grave site in Yang Ling, is similar to that on the terracotta soldiers.18 The pigment layer on top of the highly tension-ridden lacquer ground is matte and water soluble, as on the terracotta figures.

Through studies in Munich the following pigments could be identified on the polychromy of the terracotta warriors: natural cinnabar, malachite and azurite as natural pigments; bone white19 and so-called Han purple as artificial pigments.20 This is the earliest documented use of Han purple in China. It is unknown in European painting.

The pigments are variously used: there are layers of pure pigments as well as layers of pigments with small amounts of additives and layers of 'true' mixtures. Cinnabar was used without mixing for the reds. Small additions of cinnabar were found in the malachite on the green tints on the armor. Some white layers on the garments contain Han purple. The flesh tones and the purples, for example, were mixed together. Typical for all the flesh tones is the peculiar thickness of the layer (up to 0.20 mm), probably necessary to cover up the dark coloured ground. The number, colour and strength of the layers vary on the flesh tones (colour plate IV, fig. 1-7).

The following layers were identified on fragments with flesh tones:

- The flesh tones on a hand21 are applied in two layers over the ground; the lower layer is white and very thin, the upper one pink and thick.
- The finger22 of a different figure has a thin orange layer below and a thick layer of pink pigment above.
- Over a thick orange-coloured layer23 (bone white and cinnabar) there is a thin, light pink layer.
- On one fragment the pink-coloured flesh shows a homogeneous pink-colored matrix consisting of a few grains of red pigment and white "chump". Bone white and cinnabar are documented. The rose-coloured matrix is achieved using extremely finely ground cinnabar. Coloursants materials in the flesh layers have not yet been identified.

Observations on the Use of Pigments in Ancient China

The following overview on the use of pigments is based on an analysis of the rather limited literature that is available and draws parallels to western painting techniques.

Cinnabar

As a pigment cinnabar (Chinese: tansha) is already documented in the Shang Dynasty (ca. 1650-1050 BC) on incised inscriptions on oracle bones,24 there is evidence of the use of cinnabar on lacquerware from the Zhangguo Dynasty (480-221 BC). The largest deposits of cinnabar are to be found in China and Japan.25 The highest quality, chensha, was found in Chenzhou (Hunan Province).26 The 'magic elixir' (Chinese: pu su chih is'sao)27
cinnabar was an extremely important material in ancient Chinese culture and alchemy.39 Liu An (179-122 BC/Western Han Dynasty) already knows that "red cinnabar is in truth mercury."40 The extraction of mercury from natural cinnabar was also known to the Romans in the first century BC. Vitruvius reports "When the veins of ore are excavated many drops of mercury separate out as a result of flows from the iron tools; they are immediately collected by the miners ... When the ore has been taken out of the oven the little drops of mercury that are precipitated cannot be collected individually because of their small size but rather are swept together into a vessel with water; where they combine, flowing together into a mass."41

According to Wang Kuike, the artificial production of cinnabar from mercury and sulfur — synthetic cinnabar (Chinese: yinzhu) — is "probably one of the earliest chemical compounds created by man. It can be counted among the most remarkable achievements of early chemistry."42 In the book of Master Baopu (284-364) Ge Hong reports that "cinnabar; if it is heated, results in mercury, which after many transformations regresses to cinnabar again."43 More detailed information on the relationship of mercury and sulfur and their synthesis into cinnabar is found in the Tang period (618-907) in the "Metamorphosis of Mercury."44 Around this time the Chinese discovery became known in Europe, via Arabian culture.

It is not possible to establish exactly when man-made cinnabar first began to be used in place of natural cinnabar in painting; the use of artificially manufactured cinnabar is documented on red lacquerware in the Ming Dynasty (1368-1644).45 Cinnabar is unknown in ancient Egyptian painting46 and in the early Mesopotamian cultures.47 There iron oxides such as hematite and burnt yellow earth served as red pigments.48 Egypt did not have any cinnabar deposits. In Persia, on the other hand, natural mercury sulfide and hematite have been found on painted architecture, for instance in Persepolis (c. 520-330 BC).49

In contrast to China, where natural cinnabar is already known as a painting material in the Shang Dynasty (1650-1050 BC), in the West the mineral was discovered around 400 BC, according to historic sources. In his Naturalis Historia Pliny the Elder quotes Theophrastus48, according to whom cinnabar was "discovered by the Athenian Kallitas (405 BC), who originally hoped to be able to melt a red stone from the silver mines into gold. But cinnabar was already found in Spain at that time, although in a harder and sandier state ... The Greeks call cinnabar dragon's blood (kinn...baris) ... That is also what they [the Greeks] call the manure-like liquid of a dragon squashed by the weight of a dying elephant, when the blood of the two animals mixes ... There is however no other pigment in painting that renders blood so characteristically."50

According to Rhooumpolous,51 cinnabar (also called 'minium' in classical sources) was already used before the time of Theophrastus; the pigment has been documented on polychromed limestone figures from the 6th century BC in the Acropolis Museum in Athens. Cinnabar was very popular with the Romans and was not only one of the "inter pigmenta magnae auctoritatis," but rather also had ritual significance.52 The pigment is documented in Pompeii.53 Deposits were located in Spain and Ephesus.54 According to Pliny the Elder cinnabar was mainly imported by the Romans from Sisape in Spain, but it had to be processed in Rome. "It is not permissible to finish and render the cinnabar in Spain; the crude ore is brought sealed to Rome, about 2000 pounds a year."55 According to Pliny the highest quality cinnabar was found in Ephesus.

**Malachite and Green Copper Pigments**

In the Qin Dynasty (221-206 BC) the pigment malachite (Chinese: kongqing, shih lu) is documented not only on the polychromy of the terracotta army but also for instance on the wall paintings in Xianyang (Shaanxi Province).56 The malachite used to paint the terracotta figures is pure; the copper carbonate does not contain chloride. In the Mogao grottos in Dunhuang (Gansu Province) the use of malachite as well as of atacamite as a green pigment is proven.57

According to Yang Wenhe, copper ores were mined on a large scale in China already before the 11th century BC.58 In 1974 a copper mine from the Spring and Autumn era (770-476 BC) was found on Tonglue Mountain in Daye, in Hubel Province southeast of Wuhan Province: a rich deposit that contained large amounts of malachite in addition to chalcoite.59 According to archaeological discoveries from other pits in this mine, it is certain that the mine was worked from the Age of the Warring States up until the Han era, i.e., from the 5th century BC until the 3rd century AD.60 During the Song Dynasty (960-1127) malachite was recovered on the You River (Jangxi Province).61 Further deposits are found in Huize, Dongchuan and Gongshan in Yunnan Province.62

In the West the copper deposits on Cyprus63, in the Sinai64 and in Armenia65 were famous; this is also the source of the term 'armentum'66 used by classical authors for the green pigment. An early use of malachite in Egypt is documented on the wall paintings of the 4th Dynasty (2600-2423 BC) into the period of the New Empire (1580-1085 BC).67 In Europe the pigment is found in Pompeii68; in Persia in Persepolis (520-330 BC)69. In Pliny malachite is described under the term chrysocolla.70

Today there are doubts concerning the documentation worked out c. 30 to 40 years ago regarding the historical distribution and use of malachite.71 Recent investigations more and more frequently document copper carbonate with a chloride content. The presence of atacamite has been variously interpreted: on the one hand it is assumed that the chloride-containing copper mineral is a reactive product from malachite72 or also from Egyptian blue and Egyptian green73; on the other hand, that natural or synthetically manufactured74 copper compounds with a chloride content were used as green pigment.

**Blue Pigments**

In early China probably only azurite (Chinese: hence) was used as a natural blue pigment.75 Azurite was employed in painting by at least 250 BC, as evidenced by the polychromy on the terracotta army and by wall paintings from the Qin period. Azurite is also found on wall paintings from the Yuan Dynasty (1279-1368)76 in Henan Province and on Buddhist wall paintings from the Ming era (1368-1644) in Shaanxi Province.77

Like the Egyptians, the Chinese also produced an artificial blue pigment, so-called Han blue, a barium copper silicate (BaCuSi4O10). The chemical compound of barium copper silicate is very similar to that of Egyptian blue, a calcium copper silicate compound (CaCuSi18O46).78 Vitruvius passed on the production method for Egyptian blue, which does not differ essentially from that for Han blue.79 According to Wiedemann and Bayer80 "copper sulfides were used together with barite and silica sand or quartzite to make the pigments." Barite deposits (BaSO4) can be found all over China.81 Han blue was first discovered in 1983 by

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West FitzHugh and Zychermann on painted terra-cotta from the Han era (206-220). It is not known if artificial barium copper pigments were produced before the Qin Dynasty.

According to Noll, azure and lapis lazuli "have not been found in a single case" on ancient Egyptian wall paintings. Only Spurrell finds azure on the painted eyebrows of a mummy from the Fifth Dynasty (2563-2350) and on paintings from the 18th Dynasty (1580-1314 BC). In general the dominant opinion says that there was no interest in azure in ancient Egypt because it was unstable; it was replaced by man-made Egyptian blue. The latter can be traced back to the Fourth Dynasty (c. 2600 BC), on painted stone sculptures and wall paintings. The precious recipe for the production of Egyptian blue was adopted by the Romans. Known in Latin as caeruleum aegypticum, Pompeii blue or vestorium, this blue pigment has been documented in Pompeii. Azure and lapis lazuli, on the other hand, are not found in Pompeii.

In Persia architectural fragments at Persepolis (520-330 BC) exhibit mainly Egyptian blue; only very few of the investigated fragments show azure. In contrast late archaic Greek terracotta figures are painted with azure as well as with Egyptian blue.

Purple Pigments

Only ancient China invented a purple pigment, an artificially produced barium copper silicate (BaCu5Si4O14) known as Han purple (compare the section on blue pigments). Han purple could be documented several times on fragments from the terracotta army.

A purple clay was obtained in Greece and Egypt by mixing red ochre with chalk or gypsum. The Pompeian "purpurism" of the wall paintings is an organic pigment (murex brandaris), "creta argentina" (CaCO3) served as the substrate.

Investigation into pigments and techniques used in painting the Terracotta Army continues. Future findings will no doubt reveal even more clearly the precise significance of the army and its polychromy for antique sculpture as a whole. A beginning has been made with this conference.

(translated by Margaret Will)

Notes


2 Written on a wooden writing tablet out of grave no. 4 (M 54:11) from the Qin era in the district of Yunneng Shihi (Hubei Province); in: LIN CHUNMEE, 1992, p. 24.


5 So far traces of red and green pigments representing the small button-like connecting ties on the armour have been found on the analyzed fragments. BRINKE, HAU geb/SCHULPPE, ROGER (eds.), Kunstschätze aus China. Exhibition Catalogue, Zürich/Berlin/Hildesheim/Cologne 1980/81, p. 113, describe "golden buttons ... One group of armoured warriors were given tunics with lavender-blue patterns on the collars and cuffs, dark blue pants, black armour with white rivets, golden buttons and purple cords, and black shoes with red ties. " It is not specified if this is a yellow pigment or if gold leaf was really used. The Chinese say, that there is no gilding.


7 Jiang Ling excavation site (Hubei Province). The royal city of Jiang Ling was the center of lacquer production during the Zhang Guo Dynasty. Lacquered leather armour in Japan is also mentioned by KEMMEL, OTTO: Die Kunst Chinas, Japan and Korea, Potsdam 1929, p. 761.

8 To correctly interpret the ideology of the pigments one must take into consideration the fact that, in contrast to the mighty temples of the Greeks, the terracotta soldiers were not created for a magnificen
tia publica. The army is the emperor's luxuria privata for his underground, eternal life, and it is not intended for his people or for future generations.

9 The colori floridi are: minium (cinnabar), cinnabaris (dragon's blood), chrysokolla (green acidic copper carbonate), armenium (malachite and azure), indium purpurium (indigo) and purpurism (a white extender tinted with a red pigment).


11 BERGER, ERNST: Die Maltechnik des Altertums nach den Quellen, Funden, chemischen Analysen und eigenen Versuchen, Munich 1904 (Reprint 1982), p. 79; VITRUV (MARCUS VITRUVIUS POLLIO): Decem Libri de archetectorum, First Century BC; Latin Text and Translation into German: FENSTERBUSCH, CURT; VITRUV, Zehn Bücher über Ar
chtectur, Darmstadt 1964, Liber septimum, Kap. 5 & 8. "Who among the ancients did not appear to have used cinnabar sparingly like a medicament? But nowadays whole walls are being coated with it everywhere. In addition there is copper green, purple and Armenian blue... And because they are expensive a special clause is put in the building contracts that the pigments must be provided by the patron and not by the worker."

12 KÖNIG/WINKLER (PLINIUS): The coloris austeri pigments include sinopis, rubrica (red chalk), paraconium (chalk) or ochre and atratunum (black pigments).


15 For the scientific analyses see the article by HERM in this publication.

59 AUGUSTI 1967, p. 104.


62 The fragments excavated in Persepolis come from the painted architectural elements of the terrace. The sample was taken in the Hall of the Hundred Columns: "The two relief pigments (29 and 33) and the sample from the Fogg relief (F3) were identified as malachite (CuCO₃, Cu(OH)₂), a widely occurring mineral in the upper oiled zones of copper ore deposits. It has been found in numerous ore deposits in Iraq." (STODULSKI/FARELL/NEWMAN 1984, p. 145).

63 PLINIUS Liber XXXV § 6; Liber XXXIII § 86; RIEDERER, JOSEF: Technik und Farbstoffe der frühmittelalterlichen Wandmalereien Osterreichs, in: Beiträge zur Indienforschung, Museum für Indische Kunst Berlin (4), 1977, p. 376; ROSEN-CUNDE 1984, p. 89. The name chrysocolla comes from the Greek and means "gold"-glue" because the mineral is used to solder gold. "The goldsmiths also claimed chrysocolla for themselves to solder gold and maintained that all similar green substances have their name from it." (PLINIUS Liber XXXIII, § 93). RÖMP 1983 mentions a bluish green, gel-like copper mineral (CuSiO₃, xH₂O) under the heading "chrysokoll".


65 RIEDERER 1977, p. 377: "This pigment (atacamite) could already be documented on painted Egyptian objects and on medieval wall paintings in southern Germany; suggesting that this is a widespread pigment employed in place of the less frequent malachite."


67 EL GORESY, AHMED/IASRSH, H./RAZAK, M./WEINER, KARL LUDWIG: Ancient pigments in Wall Paintings of Egyptian tombs and temples: an archaeometric project, Max-Plank-Institut für Kulturphysik, Heidelberg 1986, p. 102: that pigments with a copper chloride content "were used in the Old J Middel Kingdom (2850-1570) as a green pigment and are recognized to be also synthetic and not natural minerals (atacamite) as indicated in the literature. No application of this mineral was found in the New Kingdom (1570-715). Techniques of production are discussed."

68 RIEDERER 1977, p. 373: "In China wurde stets Azurit verwendet."


72 FENSTERBUSCH (VITRUV) 1964, Liber septimum, XI, reports on the synthetic production of this blue pigment: "The discovery of the material that can be used to produce it artificially and of the method for its production earned great admiration. Sand is so finely ground with sodium carbonate that the mixture is like a flour; copper powder is rapped into shavings with rough files and mixed with it, and then the mixture is sprayed with water so that it conglomerates. When they are dry they are put in a kiln. When the copper and the sand melt together from the force of the fire they lose their properties and take on... a blue color."


74 WIEDERMANN/BAYER 1997, p. 379, with no information on the mines.


76 Lapis lazuli is described as a precious stone in ancient Western sources, but its use as a pigment in antiquity has so far not been documented.


78 According to both PETRI and SMITH (quoted from LUCAS 1962, p. 340) however, the painting on the eyebrows was green (a "green malachite paste") and not azurite.


80 NOLL 1991, p. 209; LUCAS 1962, p. 342 and RAEHLMANN, ERNST: Über die Farbstoffe der Malerei in den verschiedenen Kunstperioden, Leipzig 1914, p. 4. According to studies by EL GORESY/JACKSH/RAZAK/WEINER 1985, p. 101, the production of Egyptian blue, a blue glass frit, was known during the Old Kingdom (2850-2052 B.C.) in Egypt: "Both are multicomponent synthetic pigments and consist of manganate (CuMn₂O₄) with variable amounts of wollastonite (CaSiO₃) with Cu; Cu-rich glass and tenebrite (CuO). They were prepared by melting a Cu-rich ingredi ANT and desert sand, sometimes at temperature below 743°C — much lower than laboratory experiments showed."

81 "The artificial production of steel blue (Egyptian blue) was first discovered in Alexandria. Later Vettorius set up a factory at Puteoli (Pozzuoli)", FENSTERBUSCH (VITRUV), 1964, Liber septimum, XI.

82 The name Vettorismum is stamped in the Egyptian blue pigment ball that was found in Pompeii. It was Vettorius who brought the recipe for the production of this pigment from Alexandria to Rome (COLOMBO 1995, p. 95).

83 "In the Pompian blue wall colour the lighter blue is produced by mixing in more of the whitish grey medium in which the blue frits are then more seldom distributed. Otherwise the glass frit here is exactly the same as in Egypt, it is also in a greyish white medium of the same nature and has the same chemical and optical properties."

84 STODULSKI/FARELL/NEWMAN 1984, p. 149.

85 BRINKMAN 1996, p. 25.

86 HERM, in this publication.


88 LUCAS 1962, p. 346.

89 AUGUSTI 1967, p. 74.
兵马俑的彩绘和颜料：兼与古代其它文明之比较

摘要

我们对出土兵马俑残片上的原始彩绘作了保护，项目进行期间，彩绘的工艺和材料得到了研究和分析。通过取得的成果，使我们今天对彩绘鲜明的色彩和工艺有了较清楚的认识。不同的肤色、画得发亮的头发和瞳仁是兵器俑的典型特征。此外，其服装强烈的色彩对比以及衣服镶边的几何纹饰也颇具特色。守卫实物不朽之魂的大军施色艳丽，为此使用的都是优质名贵的颜料。如朱砂、孔雀石、石青、雄黄、磷灰石以及人造的无机矿石（硅酸钠铜）。在彩绘中鉴别出汉紫硅酸钠铜，这是迄今为止这种颜料最早的使用。这种珍贵的颜料竟如此大量地使用，这一现象值得注意。

基于史料，以彩绘工艺为重点，将颜料在中国的使用与在古代其它文明中的使用作了比较。
秦陵铜车马彩绘及保存环境湿度条件的研究

1. 概况

一九八零年十一月，秦俑考古队在秦始皇陵西侧发掘出土了两乘大型彩绘铜车马。这两乘铜车马均为青铜铸造，由各种零部件组成，而饰有大量金银铜件。

两乘铜车马均通体彩绘，所用的颜料有朱红、粉红、绿、粉绿、深蓝、白、黑、黄等。其中以蓝、白、绿三色用量较多，颜料均为矿物质。出土时多数彩绘已剥落。彩绘色彩品种很多，但明显的特征是以白色为基调并将纹样全部绘在白色底面上。八匹马身涂有白色彩绘涂层，具有鼻孔、口腔等粘膜处施以粉红。

彩绘纹样有变相的龙纹、凤纹、云纹，各种菱花纹以及多种多样的几何纹样。菱形、方格纹等几何纹是两乘车的基本纹样，一车马车舆上的纹样，二号铜车马的车舆上的纹样，以及车架、车座、车端光彩、车窗等处图纹均是以几何纹为母题组成各种形状的几何纹样。在几何纹这种基本纹样上，秦始皇陵铜车马又突出了以龙、凤纹发展而来的变相纹绘图案。在一号车的车舆内外、车上，到处装饰着这种花纹。在白色底面的衬托下，它们上下翻腾，如云流水。黑线条的外轮廊内，填充着白、黑、朱等色的鳞甲，色彩对比协调鲜明，极富立体感。这种纹样是铜车马的主体装饰纹样，并有意识地与云纹参和，代表了皇权的神圣。

秦始皇陵铜车马其他彩绘的地方也很多，比如御官铺，身涂天蓝色龙鳍，白色的龙口，龙身则彩绘着朱红色的几何型纹样。脸、手、足涂有粉红色，再如鞍、轴、伏兽等处，涂有朱砂。整组铜马看上去华美多姿，一派富丽堂皇。彩绘对秦始皇陵铜车马起了很大的作用，它简化了造型和装饰的程序，而且彩绘层还保护了作为金属器物的铜车马本身。

2. 实验部分

2.1 秦陵铜车马结构、特征

铜车马的基材为 Cu、Sn、Pb 合金，外饰彩绘，当时已经经过防腐处理，其防腐涂层为天然石灰石。分析证实，天然树脂加上细密的白色粉末组成涂料涂于铜基体上。经阳光与空气的作用，金属表面氧化，面氧化形成膜，铜车马起到保护作用，埋入地下后，受到水分和微生物的作用，使氧化物的氧化非常缓慢地进行，其致密性和附着力下降，甚至局部脱落。出土后，由于受空气、水份、氧、微生物、光照等作用，使其不断被侵蚀，彩绘不断褪色变色甚至脱落。

伞盖上有纹饰，打磨后，发现为金黄色纹样。很像“寿金”，在空气中如氧化反应取样，可发现其表面有氧化铜，再与铜块一体。铜器表面是花纹样，由于金属会转化成保护膜，有效抵抗了环境对青铜基体的腐蚀过程。未被彩绘覆盖之处，铜器表面进行防腐处理，仍具有明显的化学性质和电化学过程所致。

我国古代彩绘多来自天然矿物颜料，在墓葬条件下，长期受水份、氧化硫化物等絮化作用，部分发生缓慢水解和氧化的破坏。根据研究，主要由于光照、CO₂及SO₂对其影响。彩绘成分为表所示。

<table>
<thead>
<tr>
<th>颜 料</th>
<th>成 分</th>
<th>说 明</th>
</tr>
</thead>
<tbody>
<tr>
<td>红</td>
<td>PbO₂, Fe₂O₃</td>
<td>未分清成分</td>
</tr>
<tr>
<td>绿</td>
<td>CuCO₃, Cu(OH)₂</td>
<td>未分清成分</td>
</tr>
<tr>
<td>兰</td>
<td>2CuCO₃, Cu(OH)₂蓝铜矿</td>
<td>未分清成分</td>
</tr>
<tr>
<td>紫</td>
<td>氧化铝</td>
<td>未分清成分</td>
</tr>
<tr>
<td>黑</td>
<td>Fe₂O₃, N₂O₅</td>
<td>未分清成分</td>
</tr>
<tr>
<td>白</td>
<td>2PbCO₃, Pb(OH)₂</td>
<td>未分清成分</td>
</tr>
<tr>
<td>墨</td>
<td>无定形碳</td>
<td>未分清成分</td>
</tr>
<tr>
<td>填料</td>
<td>高岭土、云母、粘土、蒙脱石</td>
<td>未分清成分</td>
</tr>
</tbody>
</table>

表 1. 彩绘成分

变色主要是受光、水份、CO₂、SO₂等影响，土红是相当稳定的红色颜料，光照和湿度均影响不大，但本身受氧化还原作用而变色。对于朱砂，长期光照后会变黑，但湿度影响较小。不同湿度时，朱砂变暗的比率相同。对于含铅颜料影响很大。白色（Pb(OH)₂，PbCO₃）红色（Pb₂O₃）在光照和一定湿度下会发生反应：

2PbCO₃→Pb(OH)₂+2PbCO₃→Pb(H₂O)₂→Pb₂O₃+H₂O+CO₂

另外，由于紫外线的高能量，许多可见光不能引发的反应，均可被紫外线引发。因而，光照和湿度对变色有很大影响。

铜车马的不同部位，其含铜比不尽相同。归纳起来，如表 2 。

2.2 青铜器的特点是，韧性高，熔点低，硬度大。相反，熔点高，韧性大。

有人曾做过类似实验 1。在纯铜中加 15% 的锡和铅，熔点可降到 960℃ (纯铜熔点 1083℃)，若加 25 %，可降到 800℃；纯铜的硬度 35，若加 7-9 % 的锡和铅，硬度增加到 65-70，加 9-10 %，硬度达 70-100。
表 2。铜车马构件成份。

由表 2 看出，对铜车的构件要求有良好的铸造的性能，又有一定的强度，其锡含量为 13.14 %，而马车变 7.49 %；铜锅头，要求硬度大，则锡含量为 13.79 %；连锡，引锡等部件，由细小环节组合，要求必须韧性大，其锡含量为 9.24 %，弓弦为 10.03 %。

整体合金配比，与现代青铜合金 ZQSn10 及 ZQSn6 基本相同，可见当时青铜冶铸技术已相当成熟。

2.2 湿度对秦陵铜车马彩绘的影响
2.2.1 湿度的控制
湿度是环境的一个重要因素，在一定湿度下，饱和盐溶液的蒸汽压与纯水的蒸汽压的比值称为该盐溶液的相对湿度（RH %）。利用密封的干燥剂配制饱和盐溶液，待平衡后，干燥器内的湿度将达到一定值。在一定温度下，不同盐溶液具有不同的相对湿度值，本实验室采用 WHMI 型温湿度计测定了几种盐的相对湿度值。如表 3 所示。

2.2.2 色度的测量
色度的测量色差计来测量，分别采用 SC-80 色差计，这是测量颜色变化的仪器，其原理基于国际照明委员会向各国推荐的（ZE1964X10Y10Z10）的色表系统。

自然界的红、黄、蓝称为三原色，以 X, Y, Z 来表示。测量色度实际上就是通过仪器定量检测三原色的成份。以 D65 光源照明器来模拟标准观察者对颜色的三种响应。通过运算单元进行数值处理，得到的三个刺激值为（X, Y, Z）及三者出光度（x, y, 1, a, b）而定量地确定色度值，由仪器来判断颜色的差异，而得到色差值的数据。

$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$

$\Delta L$ 明度差；$\Delta a$ 红绿度差；$\Delta b$ 黄蓝度差。

由 L, a, b 三值可组成色空间，从空间的三点距离差，就可以表示出颜色的色差，通过制作色度—色差曲线，即可判断在那种湿度下颜色变化（即ΔE）最小，为最佳环境。

2.2.3 湿度对颜色的影响
通过定期测量的彩绘板，得到测量值，经过运算，得到ΔE 值。如表 4。

以表 4 中ΔE 对 RH%作图。得图 1，图 2。

表 3。湿度的控制。实验结果与文献报道相吻合。

<table>
<thead>
<tr>
<th>温度</th>
<th>项目</th>
<th>K_2SO_4</th>
<th>(NH_4)_2SO_4</th>
<th>NaNO_3</th>
<th>NaNO_2</th>
<th>Na_2Cr_2O_7</th>
<th>2H_2O</th>
<th>K_2CO_3</th>
<th>MgCl_2·6H_2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>理论值</td>
<td>96</td>
<td>81</td>
<td>72.8</td>
<td>63</td>
<td>54</td>
<td>43</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>测量值</td>
<td>92</td>
<td>83</td>
<td>73</td>
<td>63</td>
<td>56</td>
<td>47</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S 热 (g)</td>
<td>13</td>
<td>78</td>
<td>94.9</td>
<td>87.6</td>
<td>177.8</td>
<td>113.7</td>
<td>56.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S 热 (g)</td>
<td>14</td>
<td>83</td>
<td>100</td>
<td>92</td>
<td>280</td>
<td>117</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td>20°C</td>
<td>理论值</td>
<td>97</td>
<td>81</td>
<td>74</td>
<td>66</td>
<td>55</td>
<td>44</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>测量值</td>
<td>92</td>
<td>82.5</td>
<td>74</td>
<td>66</td>
<td>54.4</td>
<td>46</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S 热 (g)</td>
<td>11.1</td>
<td>75.4</td>
<td>87.6</td>
<td>80.8</td>
<td>177.8</td>
<td>110.5</td>
<td>54.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S 热 (g)</td>
<td>12</td>
<td>78</td>
<td>93</td>
<td>86</td>
<td>280</td>
<td>115</td>
<td>320</td>
<td></td>
</tr>
</tbody>
</table>
2.2.4 结果讨论
2.2.4.1 综合分析图1、图2得到湿度对ΔE影响。

白色颜料
(1) 由图1A知，在光照条件下，不同湿度导致色度不同。在较干环境中（RH%在33-55%），随RH%增大而ΔE减小，当RH%达55%时，ΔE为最小。在高湿环境中（RH%=55-81%），总的趋势是ΔE随RH%增加而增大。在97%接近饱和湿度时，ΔE反而大大降低。

(2) 由图2A知，在无光照时，除97%湿度时产生霉变，引起强烈色变外，ΔE随RH%增大而缓慢上升。
综上，选择RH%在44-55%变化最小。

红色颜料
由图2B知，ΔE随RH%的变化与白色颜料基本相同。在RH%为33-81%时ΔE值变化不明显。只是在97%时，由于霉变而导致ΔE的突变。所以，在44-55%仍变化较小。

绿色颜料
在图2C中，33-81%的湿度范围内，ΔE值基本不变。在高湿条件下，由于紫外线的杀菌防霉作用，使图1C没有太大的变化。而图2C则ΔE巨变，因此，湿度范围在44-81%范围内，对绿色颜料亦适用。

褐色颜料
湿度与光照对ΔE值影响，与绿色类似。

2.2.4.2 影响彩绘颜色变化的因素很多。在洁净环境中，忽略化学物质和灰尘的破坏作用，其色变主要是受光照和环境湿度的影响。

(1) 对光敏感的颜料，特别是紫外线，将使颜料发生化学反应。以铅丹为例：
当在紫外光照射下，铅丹吸收光能变成激发分子PbO_2*，从而具有较高的能量，降低了反应活化能，使得原来不易发生的反应可能发生。在湿度较高时，单位体积里含
有的水份较多，就使得水分子和激发态的 PbO₂*分子碰撞的机会增大，从而发生反应。干燥条件下，水份少，碰撞机会减小，难以发生反应，铅丹不变色。但湿度太高，虽然水份多，且单位体积水分子浓度高，吸收紫外光也越多。实验结果如表 5：

<table>
<thead>
<tr>
<th>RH %</th>
<th>254 nm 紫外线辐照度 (μw/cm²)</th>
<th>420 nm 紫外线辐照度 (μw/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
<td>4.8</td>
<td>20.1</td>
</tr>
<tr>
<td>66</td>
<td>5.7</td>
<td>29.8</td>
</tr>
<tr>
<td>33</td>
<td>5.9</td>
<td>33.4</td>
</tr>
</tbody>
</table>

表 5. 不同湿度的紫外线。

因此，高湿(例如 97% 相对湿度时)，由于水份吸收紫外光太多，使得穿过空气到达颜料表面的紫外光辐照度降低，阻止了激发态 Pb3O4 的生成，故也难以发生变色反应。

变色过程应是：

\[
Pb_{2}O_{4} \rightarrow Pb_{2}O_{4}^{*} \rightarrow Pb_{2}O_{4}^{2-} + PbO_{2} (\text{氧化反应})
\]

变色反应在湿条件，水和空气中的 CO₂ 参与的氧化还原反应。其依据是：铅丹可以看成由 PbO 和 PbO₂ 组成。由铅丹变成铅白可看成是 PbO₂ 被还原生成了 2PbCO₃ 和 Pb(OH)₂。

查手册知：

\[
PbO₂ + 4H_2O + 2e^- \rightarrow Pb^{2+} + 4OH^- E^0 = 1.455V
\]

根据 $\log K_{SP}(PbCO_3) = 13.13$, 由公式算出 $E^0_{PbO_{2}/PbCO_3} = 1.685V$, 并且光照使 PbO₂(PbO₂) 活化，反应向越易向右进行。从 Pb₂O₅/PbCO₃ 电对的电位变得更正，因此 PbO₂ 足以使水分氧化，本身被还原成二价铅，再和空气中的 CO₂ 结合，生成 PbCO₃。

由此分析，实验中白色和红色两种彩染的色变，由于发生了以上的光化学反应，使其 $\Delta E$ 值起伏较大，即色变最显著。

(2) 在没有光照条件下，湿度对颜色变化影响不大，只是在接近饱和湿度时，由于霉变使 $E_{AE}$ 值增大。

在光照条件下，湿度对颜色变化影响很复杂。一方面，湿度增加，色差增大；另一方面，湿度增加，对紫外线吸收增多，减小了光的波长，而色差反而减小，两者的综合影响，决定了对颜色改变的程度。

由此实验亦可看出，对光敏感的红白两种颜料均有此规律。图 3。

对光稳定的褐、绿两种颜料，在很宽范围 RH % 不影响色差。只在十分潮湿环境中，由于霉变而强烈改变其 $E_{AE}$ 值。

通过以上讨论，确定湿度数值为 44-55 %，这样就在防止了干燥条件下彩染的脱色，又防止了高湿条件下，彩染长霉。并且在此 RH % 范围彩染的色彩的改变最小。

图 3. 不同湿度下的彩染色变情况。

左图 : RH 81% ；右图: RH 43 %。

2.3 青铜器的腐蚀

2.3.1 腐蚀条件的选择

青铜器腐蚀的基本条件是潮湿环境、可溶性氯化物和氧化气氛。

可溶性氯化物是加速青铜器腐蚀的主要因素。本文对处理好的样品浸泡于不同浓度的氯化钠溶液中，进行液相腐蚀，以光度法测其腐蚀速度。如表 6 和图 4。

图 4. NaCl 百份含量与腐蚀速度(吸光度以 A 表示)。

由图知，3 % NaCl 溶液，青铜器腐蚀率最高，所以本实验选择 3 % 的 NaCl 溶液加速腐蚀试验。作者近来研究了青铜器的腐蚀机理，认为大气污染是青铜器腐蚀的重要因素。并测定了秦陵地区的大气状况，如表 7。

图 5. 不同湿度下的彩染色变情况。

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可溶性氯化物是加速青铜器腐蚀的主要因素。本文对处理好的样品浸泡于不同浓度的氯化钠溶液中，进行液相腐蚀，以光度法测其腐蚀速度。如表 6 和图 4。

图 4. NaCl 百份含量与腐蚀速度(吸光度以 A 表示)。

由图知，3 % NaCl 溶液，青铜器腐蚀率最高，所以本实验选择 3 % 的 NaCl 溶液加速腐蚀试验。作者近来研究了青铜器的腐蚀机理，认为大气污染是青铜器腐蚀的重要因素。并测定了秦陵地区的大气状况，如表 7。
<table>
<thead>
<tr>
<th>NaCl %</th>
<th>0.1 %</th>
<th>1.0 %</th>
<th>3.5 %</th>
<th>5 %</th>
<th>10 %</th>
<th>15 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.23</td>
<td>0.29</td>
<td>0.41</td>
<td>0.34</td>
<td>0.20</td>
<td>0.07</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>0.29</td>
<td>0.42</td>
<td>0.37</td>
<td>0.23</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>0.28</td>
<td>0.34</td>
<td>0.43</td>
<td>0.36</td>
<td>0.24</td>
<td>0.10</td>
</tr>
<tr>
<td>平均值</td>
<td>0.253</td>
<td>0.306</td>
<td>0.420</td>
<td>0.356</td>
<td>0.223</td>
<td>0.083</td>
</tr>
</tbody>
</table>

表 6. 不同浓度 NaCl 腐蚀溶液的吸光度 (A)

<table>
<thead>
<tr>
<th>次数</th>
<th>项目</th>
<th>SO₂ (mg/m³)</th>
<th>NO₅ (mg/m³)</th>
<th>降水 (T/km²·月)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.057</td>
<td>0.078</td>
<td>26.45</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.059</td>
<td>0.080</td>
<td>26.48</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.053</td>
<td>0.082</td>
<td>26.60</td>
</tr>
<tr>
<td>均值</td>
<td></td>
<td>0.056</td>
<td>0.080</td>
<td>26.50</td>
</tr>
</tbody>
</table>

表 7. 秦陵地区大气监测结果

<table>
<thead>
<tr>
<th>RH %</th>
<th>ΔM(mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>4.1</td>
</tr>
<tr>
<td>43</td>
<td>5.1</td>
</tr>
<tr>
<td>54</td>
<td>5.1</td>
</tr>
<tr>
<td>63</td>
<td>15.0</td>
</tr>
<tr>
<td>72.8</td>
<td>32.0</td>
</tr>
<tr>
<td>81</td>
<td>40.1</td>
</tr>
<tr>
<td>96</td>
<td>48.5</td>
</tr>
</tbody>
</table>

表 8. 不同湿度下样品的失重量

<table>
<thead>
<tr>
<th>RH %</th>
<th>Cu²⁺含量 (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>13.5</td>
</tr>
<tr>
<td>43</td>
<td>15.0</td>
</tr>
<tr>
<td>54</td>
<td>17.5</td>
</tr>
<tr>
<td>63</td>
<td>21.5</td>
</tr>
<tr>
<td>72.8</td>
<td>34</td>
</tr>
<tr>
<td>81</td>
<td>39.5</td>
</tr>
<tr>
<td>96</td>
<td>42.5</td>
</tr>
</tbody>
</table>

表 9. 不同温度下腐蚀溶液的吸光度

<table>
<thead>
<tr>
<th>RH %</th>
<th>Cu²⁺含量 (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>13.5</td>
</tr>
<tr>
<td>43</td>
<td>14.5</td>
</tr>
<tr>
<td>54</td>
<td>18.1</td>
</tr>
<tr>
<td>63</td>
<td>22.2</td>
</tr>
<tr>
<td>72.8</td>
<td>33.1</td>
</tr>
<tr>
<td>81</td>
<td>36.5</td>
</tr>
<tr>
<td>96</td>
<td>39.0</td>
</tr>
</tbody>
</table>

表 10. 不同湿度环境中腐蚀溶液的 Cu²⁺含量 (AAS)

<table>
<thead>
<tr>
<th>RH %</th>
<th>ΔM(mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>5.0</td>
</tr>
<tr>
<td>43</td>
<td>6.1</td>
</tr>
<tr>
<td>54</td>
<td>6.3</td>
</tr>
<tr>
<td>63</td>
<td>29.0</td>
</tr>
<tr>
<td>72.8</td>
<td>35.1</td>
</tr>
<tr>
<td>81</td>
<td>47.3</td>
</tr>
<tr>
<td>96</td>
<td>62.0</td>
</tr>
</tbody>
</table>

表 11. 不同温度下的失重

<table>
<thead>
<tr>
<th>RH %</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>0.255</td>
</tr>
<tr>
<td>43</td>
<td>0.270</td>
</tr>
<tr>
<td>54</td>
<td>0.295</td>
</tr>
<tr>
<td>63</td>
<td>0.475</td>
</tr>
<tr>
<td>72.8</td>
<td>0.485</td>
</tr>
<tr>
<td>81</td>
<td>0.535</td>
</tr>
<tr>
<td>96</td>
<td>0.585</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A</th>
<th>Cu²⁺含量 (µg/ml)</th>
<th>AAS 分析 Cu²⁺含量(µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>18</td>
<td>15.6</td>
</tr>
<tr>
<td>A</td>
<td>19.0</td>
<td>17.4</td>
</tr>
<tr>
<td>A</td>
<td>21.0</td>
<td>19.5</td>
</tr>
<tr>
<td>A</td>
<td>35.5</td>
<td>31.0</td>
</tr>
<tr>
<td>A</td>
<td>36.5</td>
<td>36.5</td>
</tr>
<tr>
<td>A</td>
<td>40.5</td>
<td>38.5</td>
</tr>
<tr>
<td>A</td>
<td>44.8</td>
<td>44.7</td>
</tr>
</tbody>
</table>

表 12. 不同湿度下产物的 Cu²⁺含量
2.3.2 青铜样品在酸性条件下模拟试验
A) 重量法：将样品在设定环境中放置两周后，观测腐蚀失重与 RH % 的关系，如表8所示。

![Fig. 5. Relation of time of corrosion to ΔM and to RH % (weight method).](image)

图 5. 腐蚀速度与ΔM 与 RH % 的关系 (重量法)。

B) 分光光度法：将收集到的腐蚀液用光度法测 Cu²⁺ 含量。如表9和图6。

![Fig. 6. Relation of time of corrosion A % to RH % (spectrophotometric method).](image)

图 6. 腐蚀速度 A % 与 RH % 关系 (分光光度法)。

C) 原子吸收法
将腐蚀产物收集于 25ml 比色管中，用 AAS 法测定如表10和图7。

![Fig. 7. AAS Analysis Cu²⁺ content.](image)

图 7. AAS 分析 Cu²⁺ 含量。

2.3.3 样品在 NaCl 溶液中的腐蚀
同样用重量法、光度法、原子吸收度，观察腐蚀结果，如表11和图8、表12和图9、图10表示。

![Fig. 8. Relation of time of corrosion to RH % (weight method).](image)

图 8. 腐蚀速度与 RH % 关系 (重量法)。

![Fig. 9. Relation of time of corrosion to RH % (spectro photometric method).](image)

图 9. 腐蚀速度与 RH % 关系 (光度法)。

![Fig. 10. Relation of time of corrosion to RH % (AAS method).](image)

图 10. 腐蚀速度与 RH % 关系 (AAS 法)。

2.3.4 气相腐蚀实验
亦采用重量法、光度法观察腐蚀速度，如表13和图11、表14和图12。

表 13. 腐蚀速度与湿度关系。

<table>
<thead>
<tr>
<th>RH %</th>
<th>34</th>
<th>46</th>
<th>58</th>
<th>75</th>
<th>96</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1% SO₂ 存在时 ΔM(mg)</td>
<td>1.1</td>
<td>1.1</td>
<td>1.2</td>
<td>2.9</td>
<td>4.0</td>
</tr>
<tr>
<td>0.1% SO₂ 及 3% NaCl 存在时 ΔM(mg)</td>
<td>1.2</td>
<td>1.2</td>
<td>1.6</td>
<td>3.5</td>
<td>4.8</td>
</tr>
</tbody>
</table>

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大气腐蚀时，当相对湿度小于 50 % 时，此时的液膜厚度不足以实现氧化还原过程，因此腐蚀程度小，当相对湿度大于 70 % 时，氧化通过液膜传递到金属表面的速度加快，加速了腐蚀。

3) 在 SO₂浓度一定的条件下，温度和湿度是影响青铜腐蚀的重要因素。温度的影响主要是水蒸汽的凝结，凝结水膜中各种腐蚀性气体和盐。当相对湿度低于金属临界相对湿度 (<65 %) 时对腐蚀的影响很小，而当相对湿度达到金属临界相对湿度时，温度的影响很大。

3. 结论

1) 研究了相对湿度、光照和彩绘脱色之间的关系。在无光照情况下，湿度对彩绘脱色影响不大。只有在高湿情况下，由于霉变而影响Δ值。而在有光照时，由于湿度和紫外线间的关系，对光敏感的含氯颜料（红、白），湿度应控制在 44 % - 55 % 范围内。对于褐、绿两种适用湿度范围较宽的颜料来说，中等湿度下，其色变值ΔE 亦较小。

2) CuCl₂是极不稳定的化合物，它可以在水蒸气、氧气、酸性条件下，氧化氯化铜矿和氯化铜矿 [Cu₂(OH)₂Cl₂]，通过XRD分析可知：随相对湿度的增大，Cu(OH)₂Cl₂的衍射峰强度也增大，在相对湿度 72.8 % 左右时，转变有突跃值。

3) 在 20°C 和通常在大气压下，湿度大于 63 % 时，NaCl 将与 Cu₂O 作用而生成 CuCl₂·Cu(OH)₂，此作用亦随相对湿度的增大而加剧，因此，青铜器表面附着层表面质变的氯化物，会对 Cu₂O 起破坏作用。

4) 在模拟实验中，当 pH 值较低时，粉状锈生成趋势较快，速度随相对湿度增大而增大，临界相对湿度值在 70 % 左右。在有吸湿性盐类存在的情况下，由于 CT 的大量存在而加剧，且腐蚀途径有所改变，导致临界相对湿度有所降低(60-70 %)，促使锈蚀介质更易发生，程度加剧。

5) SO₂对青铜腐蚀的影响。主要由于它在吸附水膜下参加了酸性的去钝化作用。在模拟大气 SO₂含量的气相腐蚀实验中，青铜样品的腐蚀随温度的升高而加剧，随湿度的增大而加速。

2.3.3 结果讨论

1) 由 Cu₂O 生成粉锈的过程中较为缓慢，但在酸性条件下及 CT 存在下发生此种反应，当湿度大于 66 % 时，能够溶解氯化钠所需湿度，此种转化有一突跃值，表明 CT 直接破坏了氧化亚铜层。

2) 通过模拟实验可知，青铜在没有外来电解质作用下时，主要受氧的缓慢作用生成 Cu₂O，在酸性条件下，Cu₂O 则随环境湿度的变化逐渐转变为氯化铜矿(粉状锈)。此种转变在相对湿度 70 % 时有一突跃，一方面是由于青铜吸附水膜所致，另一方面由于 H⁺的存在，使 Cu(OH)₂Cl₂更易生成。

注：
1. 文摘: 《文物保护技术》，6，51 (1991)。
2. Handbook of Chemistry and Physics (下册)，1596-1601 (1953)。
3. 程瑞勇: 《西北大学学报》，1，30 (1989)。
The Polychromy of the Bronze Chariots from the Mausoleum of Qin Shihuang

The bronze chariot unearthed from Qin Shihuang's mausoleum is eulogised as "the champion of bronze wares", for it is the biggest of its kind ever unearthed in China. Its surface is painted with mineral pigments whose major colours are white, red, green, etc. The brilliant patterns effected with the colours truly reflect the original look of the chariot. After being excavated, the paint layer began to peel off due to the sudden fluctuation of temperature and humidity. Very important here is an ideal environment to protect the chariot after a careful analysis of the pigment ingredients, a careful study of how the bronze alloy eroded and the paint layer has changed under different simulated conditions has taken place.

Simulated experiments show that the fading of colour is related to environmental humidity, the ultraviolet illuminant and the pigment variety. The chromatic aberration value (DE) of 4 pigments under different humidities determines the best humidity range of 44 to 55%.

The corrosion products of the chariot have been analyzed by X-ray diffraction, which reveals that CuCl is the key factor of bronze ware corrosion. The three basic conditions that influence the corrosion are (1) damp environment (2) oxidised atmosphere and (3) soluble chlorides. A series of experiments have been done to determine the suitable temperature and humidity in which CuCl and Cu₂O changes into powder rust. Simulated experiments tested the correlation between the corrosion speed and the change of external conditions. Sample bronze wares were put under 7 kinds of surroundings of different humidity. As a result, the suitable natural conditions have been suggested for the preservation of bronze wares.
Symbolism and Meaning of Colours in Early Chinese Sources

What did colour mean to Chinese people more than two thousand years ago? Written sources seem to tell a different story regarding this subject than the archaeological record shows. Indeed, it is not very probable that there will be much agreement between the answers which philology and archeology can give to this question. Nevertheless, it remains important to look at texts when trying to understand why certain colours were displayed more prominently in ancient Chinese art than others. There is the possibility that, as in other cultures, sculptures were not designed to represent real life but to comply with ideals about how humans should look. Today such ideals can only be revealed by reading texts, not by looking at physical objects. However, this essay refrains from explaining why certain colours were used more often than others. Limited as our knowledge still is, such an attempt would for the time being certainly be doomed to failure. Therefore, this paper will confine itself to giving an idea on basic Chinese concepts concerning colours to those who are not acquainted with ancient Chinese sources.

Colour Terms

For several reasons Chinese colour-terms are interesting with regard to the subject of this paper. The most important reason to study terminology is that the graphs used to describe colours in ancient China can tell us a lot about the early development of Chinese culture. However, as there have been numerous very different interpretations of the original meaning of ancient Chinese characters, mainly by Chinese and Japanese scholars, the reader of the following lines should be aware that he is treading on very thin ice. Many assumptions about the meaning of ancient graphs do not go beyond the level of speculations.1

As early as at the time when oracle bones were inscribed at the end of the second millennium B.C. colours seem to have been important as part of the ritual system of the Shang. Apparently, even at this early date the use of colours sometimes related to a specific context. White, red and multi-coloured oxen were, for example, frequently sacrificed in the ancestral cult whereas black sheep were used in rain-making rituals. Yellow oxen seem to have been sacrificed mainly to the directions or to earthly gods.2 Recent research suggests that the colour system of the Shang consisted of only four basic colour terms: those for red, white, yellow and dark.3 The element which is certainly mentioned most often is red for which there are at least three different terms, namely chi 紅 which is used mainly to designate the colour of horses, xing 赤, which probably means yellowish-red close to orange and describes the colour of oxen, and xuan 紫 or you 深, both of which seem to be words for a darkish red colour. Although xuan in later times came to be used for “purple” this cannot have been the original meaning of this character since in oracle bone inscriptions it is the colour of a dark oxen.

The character for the word “chi” is composed of the elements of a human figure, which was later, when the writing system developed, stylized as “da”, big, and of fire. It is not clear, however, whether we have to conclude that the human figure gave a semantic meaning to the character as did the element of fire or whether it was only a phonetic element of the graph.4 In the case of xing it seems plausible to assume the latter, namely that one of the two elements which means “sheep” is a phonetic one whereas only the other element “oxen” gave a semantic meaning to the character. Xing, then, would simply be the normal colour of an oxen. Similarly to chi the character “you” seems to be composed of an element which represents fire (although the modern written form looks like the character for mountain) and a phonetic element which is the same that is also used for writing the other character meaning dark red, namely xuan. Other words for red, such as zhu 赤, a character which seems to be a graph of a tree from the trunk of which a red dye-pigment is obtained,5 or dan 黑, cinnabar, do not occur as colour terms in the oracle bone inscriptions. Hence, it seems that the use of these terms dates to a later time. Dan has been thought to be drawing of a globule of mercury on a pan or of a lump of mineral in a crucible.6

Hei 黑, the modern word for black, does occur in oracle bone inscriptions in sentences such as: “We do not use black sheep, there will then be no rain” or “we should sacrifice black dogs, the king will then receive assistance”. It seems also to have been used for the word “drought” which may have been phonetically close to “huang” 黃, yellow. This might be the reason for the fact that yellow and black are sometimes confused in the inscriptions. The character has been interpreted as a drawing of a human figure with face and body covered with spots of dark war-paint or with a tattooed face, a punishment of criminals.7 As has been pointed out, however, the bone graph does not have the ink spots which occur only in the later bronze-inscriptions and there the character is never used as a colour term.8 It is, therefore, more plausible, that the pictograph for black shows two snot-collecting vessels over a chimney.9

According to two eminent Western scholars, huang, yellow probably shows a man with a large belt10 or with gold nuggets.11 However, Gao Hanyu says that the old graph for yellow clearly contains the character “fire” which suggests that this, again, is a character which was used to describe one of the colours of fire.12 In oracle bones it describes most often the colour of oxen but sometimes also of bronze or gold.

There are several theories concerning the character for “bai” or “bo” meaning white, all of which have been rejected by modern scholars. There are not many convincing explanations at the moment for what this character may have represented.13 As an example how complicated the business of interpreting characters can become, note the interesting explanation by Ulrich Unger who thinks that bai originally represented an acorn and was only later used as the word for “white” because of its phonetic value. Later it was incororated into the character for “oak” (li 李).14

Interestingly, there is no term for green or blue in the oracle bone inscriptions. Although the character qing 青 which has
been explained as showing a plant, possibly indigo, with its juice being collected in a pan; does occur in these inscriptions, it is never used as a colour term - which makes this explanation implausible as far as early times are concerned. The character is, however, phonetically and graphically related to sheng, "to grow". Although there is ample archaeological evidence for the fact that the Shang knew the colour green, the lack of the colour-term "green" or "blue" on oracle bones seems to suggest that most probably there was no term for blue or green at that time and that this colour was subsumed under the category of "dark", "yellow" or "multicoloured". There is, however, also the possibility that there was a word for "blue" or "green" but that it was not mentioned because colours were usually referred to in these inscriptions in relation to sacrificial animals - and that there was simply no blue or green sacrificial animal. With regard to this problem it is, on the other hand, significant that, in a commentary to the Book of Changes, which might date back as late as the third century B.C., heaven is "xuan", dark, contrary to the earth's being yellow. It seems that the colours blue and green were latecomers, which emerged from the dark category from which, much later, the modern terms "liu" 綠, green, and "lan" 青, blue also derived. The use of the terms "qings" or "cang" 青 for the colour of heaven in other texts also seems to be late against the passage in the Book of Changes which reflects the earlier situation.

A most interesting word is in our context the Chinese word for "thing", wu 呈 which obviously originally consisted of two words, one clearly being an oxen and the other one meaning "multicoloured". This fact has been pointed out as early as the beginning of this century (by the noted scholar Wang Guowei)15. In China's first etymological dictionary, the Shuowen of Xu Shen 許慎, which was written at the turn of the first to the second century A.D. the character wu is defined as a general term for things. This usage seems, however, to start only during the late Zhou period, a fact which has led to many mistranslations of early Chinese texts by Western scholars. The part of the character which means multicoloured has been explained either as a plough breaking up earth, the meaning referring to the colour of the soil16 or as a knife with dots representing the object it cuts apart. In the latter case the opinion has been expressed that the primary meaning was "to separate" or "select".17 This interpretation is important because in some early texts "wu" quite clearly means "to select by colours". Only late the character wu developed to generally refer to a type of classification, whence it derives its meaning of "things".

For example, in the Rites of the Chou, Chou-li 周禮, which was probably written during the third century B.C. but which records a great number of ancient practices, there is mention of an official who is in charge of classifying the land in order to choose the right grain to be grown on each spot. The word for "to classify" is "wu", and it is explained by the second century A.D. scholar Zheng Xuan 鄭玄 as "to judge on colour and shape".18 Elsewhere the same commentary says that to classify means to look at the colours.19 Where the text says that it is possible to know in advance about coming disasters and catastrophies but also lucky events by watching the "categories of the five clouds", the word for category - which is again "wu" - is explained as colour. Yellow clouds mean, according to an early first century A.D. commentary, locusts, white colours mourning for a dead, red ones war, black ones monadations and yellow ones a good harvest.20 In any case it seems quite plausible that the very word for "things" is closely connected to the word for "colour".

Five Elements Speculations and the Military

With this last passage we are, of course, in the realm of Five Elements speculations which probably started during the fourth or third century B.C. We find these speculations in the Zuo zhuan 史記, a historical text narrating the events from the period of the 8th until the fifth century B.C. In this work it is said that a good ruler of men has to make a display of his "things" which consist of objects in five colours. Again, a commentary, this time from the early 3rd century A.D., explains that the chariots, uniforms and weapons are arranged in order to symbolize the ruler's power over heaven, earth and the four directions and that for this purpose they should be distinguished by the five colours, the best means to distinguish these things.21

It becomes quite clear that in the Zuo zhuan "wu", things, are a word for the emblems by which status and rank are shown22, and it seems that in this context colour played a very important role as early as at the time described in this text. For us this is important because from this time on in ritual and speculative systems colours began to become associated with certain objects or with directions. Partly we find similarities in these later systems with the early ones to be found in the oracle bone inscriptions. A relationship between the colour black and the element water can be seen in oracle bone texts (as mentioned above) as well as in five-elements theories. The same is true for the earth which is associated with yellow and for fire which - quite naturally - belongs to red. It is well-known that coloured animals were associated with directions, the green dragon being the animal or the essence23 of the east, the red bird the one of the south, the white tiger the one of the west and the black warrior - sometimes also a turtle - the one of the north.

In the Records of Rites, the Li-chi, we read the following famous text:

A fighting chariot has no cross-board to assist its occupants in bowing; in a war chariot the banner is fully displayed; in a chariot of peace it is kept folded round the pole. A recorder should carry with him in his carriage his implements for writing; his subordinates the (recorded) words (of former covenants and other documents). When there is water in front, the flag with the green bird on it should be displayed. When there is (a cloud of) dust in front, that with the screaming kites. For chariots and horsemen, that with wild geese in flight. For a body of troops that with a tiger's (skin). For a beast of prey that with a leopard's (skin). On the march the (banner with the) Red Bird should be in front; that with the Dark Warrior behind; that with the Azure Dragon on the left; and that with the White tiger on the right.24

Zheng Xuan's commentary explains that the four animals mentioned last represent the different formations of the troops. It is not clear whether the uniforms of the soldiers had to be in the relevant colour or whether there were just animals represented on the flags. One thing becomes quite clear, however, namely that colours played an important role for the military. We do not know whether the technique of wearing uniforms with distinct colours, permitting the easy recognition in battle of the men of one's own side, which was definitely used at the time of the fifth century A.D. was known earlier, but recent archaeological discoveries suggest that this development might have started as early as the fifth century B.C.25

Textual data seem to support this hypothesis. In the Mu ci 《穆》text, parts of which may be dated as early as the beginning
of the fourth century B.C. the use of corresponding colours for
dress, flags and banners, numbers, sizes, sacrifices and the like
is recommended:38

If the enemy comes from the east receive him at the
eastern altar. The altar should be eight feet high, the hall
eight feet deep (?), and there should be eight people who are
eighty years old. The host should sacrifice with a green
banner, there should be eight green spirits which are
eight feet long, sixty-four crossbows should be raised and
halted. The uniform of the general should be green, the
sacrificial animal a chicken. If the enemy comes from the
south receive him at the southern altar. The altar should
be seven feet high, the hall seven feet deep, and there
should be seven people who are seventy years old. The
host should sacrifice with a red banner, there should be
seven red spirits which are eight feet long, forty-nine
crossbows should be raised and halted. The uniform of the
general should be red, the sacrificial animal a dog.39
The text continues to make the same remarks for the west,
associated with the colour of white and the number nine, and
for the north with six and the blackboard.
Another text which describes events of the year of 91 B.C.
writes that when the crown prince of Emperor Wu of the Han
tried to overthrow the government, his army used the red
insignia of the Han. Therefore the Han added yellow pennants
in order to make it easy to recognize their own forces.41
That certain commands were expressed by the colour
of flags has been demonstrated earlier in the passage from the
Book of Rites. The Mohists developed this system further:
In general, the standard procedure for defending cities is:
Make grey-green flags for wood (i.e. if you need wood or
if there is wood for those who are in charge of wood);
make red flags for fire, make yellow flags for firewood
and fuel; make white flags for stones; make black flags
for water; make bamboo flags for food; make grey
goshawk flags for soldiers, who will fight to the death;
make tiger flags for mighty warriors; make double rabbit
flags for brave soldiers; make youth flags for fourteen
year old boys; make dog flags for crossbows, make forest
flags for halberds feather flags for swords and shields;
make dragon flags for carts; make bird flags for cavalry.
In general, when the name of the flag that you are looking
for is not in the book, in all cases use its form and name to
make [the design on] the flag.42
The Mohists obviously had handbooks for the defenders
which instructed them to decide on the colour and design of
individual flags.

Cosmological Systems and the Statecraft

It is well-known that in Five-Elements speculations there are
the elements of earth which is yellow, fire which is red, metal
which is white, wood which is green and water which is black.
In the texts just quoted only four of these elements were
mentioned, with the earth missing. Although yellow as the
colour of the centre is alluded to in early texts43 it seems that
the systematization including five colours is late and that
originally only the four directions belonged to the system.
The Discussions from the White-Tiger Hall (Boha tong), a
text which probably was written around 80 A.D., contains
another passage mentioning the four animals of the directions.
Here the yellow centre constitutes the fifth element but no
animal is mentioned. It looks very much like this fifth colour
had to be added because of the conventions of the day, but that
this could not be done in a proper way because the original set
did not include a fifth animal. That the fifth element is a late
addition which is somewhat unnatural to the old system based
on only four parts can also be seen by the fact that systematiz-
ting ritual texts of the time make the colours correspond to
the four seasons: spring which is green like the east, summer
which is red like the south, autumn which is white like the
west and winter which belongs to black and the north. The
centre is in an awkward way added to this system as the last
month of summer and the colour yellow.44 In the dictionary
Shuowen 說文 the colours are usually defined as belonging to
their directions.
There is more evidence which can serve as a basis for
our assumption that originally the Chinese colour cosmos
was constituted of only four primary colours: when the Qin
started to challenge the supreme power of the Zhou
dynasty, they step by step seem to have established a
system of sacrifices to Supreme powers whom they called
"Di" - a word which later became the designation of the
Chinese emperors. As the territory of the Qin lay to the
west of the Zhou it was only natural that the first of these
sacrifices, established in the year of 756 B.C., was directed
to the white power, the baidi 白帝, who controlled the
west.45 Eighty-four years later the Qin established a
second sacrifice to a divine power, this time the green
one.46 According to our sources in the year of 422 B.C. the
Qin added two more sacrifices to the yellow and to the red
power on high.47 No more sacrifices were added.
It is significant that, with the exceptions of the sacrifice
established first, the sites where these sacrifices took place did
in no way correspond to the cosmological prescriptions which
we know from the Record of Rites and other semiclanical
texts. The sacrifice to the white power lay northwest of the city
of Yung, the one for the blue power to its south and the two for
the red and the yellow powers to its west. This suggests that
the specifications concerning a relationship between the
directions and the colours were not universally acknowledged
during the period of the rise of the state of Qin. On the
contrary, it seems that the system was observed at the time of
Emperor Wu of the Han (140-87 B.C.) when his sons at their
enfeoffing ceremonies were presented with coloured earth
from the central altar of the earth at the capital. Each son was
given earth in a different colour, according to the direction from
the capital in which his fiefdom lay.48 The careful reader will have noticed that a black power was
missing from the adresses of the imperial sacrifices of the Qin.
The following complicated argumentation might give a reason
for this strange fact: Besides a cycle of four and of five colours
the Records of Rites also mention a dynastic cycle of three
colours, namely black, white and red. The Xia dynasty is said
to have ruled under the colour of black, the Shang under the
colour of white and the Zhou under the colour of red.49 Because one dynastic cycle was over when the Zhou declined,
the Qin were said to have again ruled under the colour of black
and the power of water. This conclusion was also drawn from
eight-elements-speculations.50 In the beginning of the Han there
was some uncertainty regarding the colour which should guide
the new dynasty. First, the founder of the Han thought that he
was the son of the red power who had killed the son of the
white power - which was quite natural because he came from
the red southern state of Chu whereas the Qin were white and
western. Only a year later, however, the first emperor of the
Han asked:
Ritual Use of Colours

So the Han, after some initial wavering, began to rule under the power of black in the same way as their predecessors whose reign over the united empire had lasted only fourteen years and who were, therefore, not taken for a real dynasty. Under the influence of cosmological speculations they later changed their colour twice, first to yellow and then to red, which had been the initial idea of the first emperor of the Han. This does not need to interest us here. What is important for the the history of the Qin is that this dynasty is said to have ruled under the element of water and to have honoured the colour of black - although elsewhere it is stated in the textual sources that the Qin officials wore white uniforms.

Needless to say that the system of adopting a colour governing the time of a dynasty has been observed ever since this time until the collapse of imperial China.

Of course, the rule to adopt a certain colour for the reign of a dynasty was only the tip of an iceberg of ritual obligations which had to be followed by officials, dignitaries and common citizens of imperial China. A fitting example for these rules is provided by the following passage which is taken from the chapter Yucao of the Records of Rites:

At the ceremony of capping, the first cap put on was one of black linen. The use of this extended from the feudal lords downwards. It might, after having been thus employed, be put away or disused.

The dark-coloured cap, with red strings and tassels descending to the breast, was used at the capping of the son of Heaven. The cap of black linen, with strings and tassels of various colours, was used at the capping of a feudal prince. A dark-coloured cap with scarlet strings and tassels was worn by a feudal lord, when fasting. A dark-coloured cap with grey strings and tassels was worn by officials when similarly engaged.

A cap of white silk with the border or roll of a dark colour was worn by a son or grandson (when in a certain stage of mourning). A similar cap with a plain white edging, was worn after the sacrifice at the end of the year’s mourning...

A dark-coloured cap with the roll round it of white silk was worn by one excluded from the ranks of his compatriots [because he had been refractory]...

An ordinary officer did not wear anything woven of silk that had been first dyed. One [dignitary] who had left the service of his ruler wore no two articles of different colours.

After these sentences which clearly show that the wearing of coloured robes was, at least theoretically, reserved for officials there follows what are usually considered the most important lines concerning the colours in early Chinese sources:

If the upper garment were of one of the correct colours, the lower garment was of the [correspondent] intermediate one. What are “correct colours”? For Zheng Xuan the “correct colour” was only one, namely xuan which can be rendered either as “black”, “dark” or “purple”. The “intermediate colour” is for him “xun 紫” which today means crimson. Kong Yingda, a seventh century commentator, explains that “xuan”, “dark” is the colour of heaven and “xun” which he glosses as a mixture of red and yellow is the colour of the earth - Heaven had to be on top, the earth underneath, as far as the robes of dignitaries were concerned. However, Huangfu Mi 黄鉅 (215-282 A.D.), another commentator, says that the “correct colours” are the five colours of the directions, namely blue, red, white, black and yellow. For the intermediary colours he mentions green, jadegreen, bay-yellow, purple and somekind of pink - a mixture of red and white.

Similar rules applied to the colours of girdles and even of knee-covers. Of course, according to the Record of Rites, the wives of officers were not allowed to choose the colours of their robes freely. They wore robes in colours which were determined by the rank of their husbands. In many later dynastic histories we find treaties with detailed prescriptions for the colours of chariots, clothing and seals.

Red

A high predilection for the colour red is to be found throughout these texts. For example, the highest seals of state always contained an element of red, the wheels of the chariots of high officials were painted red, and so were their houses. We may see here an influence of red as the kingly colour of the Zhou as well as the imperial colour of the Han - or the other way around: the Zhou and the Han may have chosen this colour because of their high social status. Two examples from the Han period relating to religious and political contexts may suffice to demonstrate this here. The Taipingjing, a Daoist text dating probably at least partly from the first and second century A.D. says:

If today the correct miasma arrives one will not for long be able to nourish evildoers. This is as if a Yang miasma arrives which has the effect that the Yin-miasma vanishes. Now if on top of utmost Yang the red miasma comes this is the essence of the fire-king. The fire-king is the sun which is the brightest [object].

The second example belongs into the sphere of semimeta-physical apologetics of the Han dynasty shortly before its final collapse at the end of the second century A.D. It is a fine example of how five elements colour symbolism was understood at that time. The end of the Spring and Autumn Annals, a chronicle of the kingdom of Lu traditionally ascribed to Confucius is explained by He Xiu in a subcommentary:

The master since long times knew... that a commoner named Liu Ji [the founder of the Han] would replace the Zhou dynasty. When he [Confucius] saw that a gatherer of firewood captured a unicorn he knew that it had come because of this [man]. Why that? The unicorn has the essence of wood [green]. A gatherer of firewood is a commoner. The meaning is that he wants to make fire [red]. This means that the red emperor was going to replace the Zhou and to take their position. Therefore the unicorn was captured by a gatherer of firewood...

After the unicorn had been captured Heaven sent down a bloodscripture and wrote at the capital gate of Lu the following words: “Quickly create laws because the sage
Confucius is going to die and the Haus Ji of Zhou will perish... When Zi Xia, a student of Confucius) the next day went to see what happened the bloodscripture flew away becoming a red bird which transformed itself into a white scripture... 48

Red, associated with magic blood was to continue to be in favour for centuries, as it is still today. That the mining of mercury, which is needed for producing the read substances cinnabar or vermilion was a very profitable business from quite early times on, is suggested by a story to be found in the second century B.C. Records of the Historian, an account of a widow from Sichuan:

There was a widow of Ba by the name of Qing whose husband's ancestors had found mercury mines and monopolized the profits for several generations. The family wealth was beyond counting. This woman had the ability to look after her enterprises, using much of her wealth as protection so that no one molested her or them. The first Qin emperor considered her a virtuous widow, treated her as a protector and caused to be built in her honour a monument called the Tower of the Women's Remembrance of Mistress Qing. 49

Because of evidence such as the one just quoted, it is quite clear that red was the dominant colour in China from very early times on. 50

Much earlier than this story was another event in which cinnabar played an important role: There is an entry in the Spring and Autumn Annals (670 B.C.) 51 which reports that the pillars in the temple where the ancestral tablet of duke Huan (710-693 B.C.) was enshrined were painted in vermilion. He Xiu explains that this was done because the son and successor of Huan was going to marry a woman from the neighbouring state of Qi and that he wanted to show off in front of Qi he probably wanted to demonstrate how much luxury he could afford. 52 It should be pointed out that together with azure cinnabar later become a word for loyalty: both materials, do not decay. None of the other materials, which are systematized in much later sources such as Wang Tao's Wai Tai biao (dating to the year of 752 A.D.), such as malachite for green, east and wood, arsenicite for white, west and metal, magnetite for black, north and water and realgar for yellow, the centre and earth seem to have played a similar role as cinnabar. 53 Apparently, yellow became an important colour for the statecourt only at the time of the Sui dynasty at the end of the sixth century A.D. It should also be noted that the Chinese did, as far as our written sources are concerned, not perceive themselves as a yellow race until very late - probably as late as the seventeenth or eighteenth if not even the nineteenth century.

Critical Statements Against the Use of Colour

Finally, all ideological characterizations of colours notwithstanding, it should be pointed out that all the attempts at systematizing certain aspects of colours must be seen in the right of a very strong sense among erudites of ancient China, that the use of colours in itself was deemed a negative thing.

A remark of Confucius runs:

"Fine words and an insinuating colour are seldom associated with true virtue," 54 a remark which is repeated thrice in the Confucian Analects. And Laozi says:

The five colours make blind the eyes of men
The five sounds make dull the ears of men,
The five tastes make apathetic the mouth of men...

Therefore the sage ... does not act for the eye. (Laozi 12)

Warning statements against the evil influence of the five colours for good government and public order are too numerous in ancient texts to be counted. What is the reason for this strange rhetoric? First of all, of course, many literati feared that too much money would be spent on things which were only superficial and not substantial. Secondly, the word for colour itself and its Chinese character provide a clue: the word "se" does not only mean "colour" but also "appearance", "cros" or simply "sex", Shen wen says that it is the "mood which is expressed in the face" 55 because "se" is used to express feelings of anger, joy and the like. One scholar even thinks that the basic meaning of the pictograph has to be interpreted as "sexual intercourse" 56 and, indeed, in later texts the character very often simply means men's desire for the opposite sex.

Confucius said: "I have never seen a person who loved virtue more than sex or the beauty of women" (L.Y. 9.18 and 15.13). It is possible that the double meaning of the word "se" results from the fact that since the earliest times women used coloured cosmetics for beautifying themselves. The word for colour could as a pars pro toto have taken the meaning of "eros". If this is true, then there would be small wonder that Chinese - philosophers, who often warned that a ruler who neglected the state business because of his appetite for material goods and sensual pleasures would eventually lead the world into ruin, despaired the use of colours altogether. This scheme could also explain why there were so many complicated rules regulating the use of colours. - Only with systematized and ritualized rubs could the negative effects, which the costly luxury of colours produced, according to the erudites be mastered.

Notes

4 Gao Han Yu, Lixiang se 1979/1, pp. 31, explains chi as the colour of a big fire.
6 Ibid. Compare Karlgren, op. cit., pp. 157, number 150.
7 Wang Tao, op cit.
8 Karlgren, Nr. 904.
10 Wang Tao, pp. 92.
凡·埃斯

从中国古代史料看颜色的象征和意义

摘要

对这篇论文的标题《从中国古代史料看颜色的象征和意义》需要作些说明。首先，这次研讨会有两篇专门探讨文字史料，而不涉及原文材料及艺术品的论文，本文即其中之一。

此种以文字为材料的论文，其范围易于限制；当然，为了推断工艺与文化的发展，使用较近的史料亦非不可，但就观念而言，这种作法无不危险。由于肇始于汉代末年，儒家不是更早的话，并至六朝(公元200-600年)两种新的宗教，即佛教和道教的出现，中国文化在这个阶段经历了大变革。鉴于此，在探讨中国古代思想史的研究中，语言学家通常将他们的注意力集中在所谓“佛教传入之前”时期的文献。这同样适用于我们的研究课题，依靠公元200年之后的材料，对生活在秦代的文人和艺术家于颜色所持的看法下结论。未免过于冒险。因为我们知道，一些颜色

在隋、唐时期和再往更早的时期乃具有不同的意义。

本文试对文字史料，即从甲骨文开始到公元一、二世纪的哲学著作，作一番审阅，目的是了解在探索不同课题时，如何中国古代颜色术语的起源、五行学说中的颜色角色，礼仪中使用的颜色或一些颜色的社会意含，这些史料究竟能提供什么帮助。另一个目的是揭示那些记载颜色的生产原料的出处，最后我想侧重讨论中文颜色名称的内涵以及文人对使用颜色的看法的转变。在西方汉学家，既无人对大部分这些课题作充分论述，也缺乏对重要材料作有条理的描述，本文唯一的希望是对材料进行初步的概括，以便大家讨论。

(英译中：陈敬林)
中国古代绘画技术及颜料

古代人类绘画的技术和颜料基本上与文字是同步发展的，到 15 世纪以后，东方与西方的绘画技术才拉开了距离。古代亚洲、中亚、欧洲各国的绘画技术是以线描、平面构图和色彩技巧为主，所使用的颜料也大体来自自然界的物质，如石墨颜料、植物颜料、矿物颜料、金属颜料以及少量的简单化学颜料等。我曾在欧洲 4 国考察过他们古代绘画，我认为欧洲的宗教题材作品，远至希腊罗马时期的绘画，还保留着很多古代的绘画痕迹，他们画家和技术所使用的颜料是十分相似的。相似的原因有三：

1. 人类绘画的原发性心态不约而同地相似的。
2. 人类绘画的，即 16 世纪以前科学不发达，画家能选择天然的有机或无机颜料。
3. 人类绘画有各地区、各洲之间的文化艺术交流。（通过丝绸之路）

关于古代文化交流，例如中国古代画家所使用的蓝色颜料（蓝青石 lapis-lazuli）就是当时从东西传过来的，🙌青色石在中国的阿富汗，是古代的丝绸之路带到中国来的，当时的色彩是这样：青色石青色为蓝铜矿硫酸。（青色为蓝铜矿硫酸）。

我曾在欧洲的巴黎、伦敦、阿姆斯特丹、布鲁塞尔等地看到了许多博物馆，重点参观西方古代的中世纪绘画，我是去寻找和东方绘画中共同的，不是去找区别的。瑞典汉学家罗多认为应该强调中西文化的不同性，如果过于强调文化的相似性，会使艺术发展的更难，我俩很高兴参加这次会议，因为它会促进世界许多国家的了解，从而找到更多的相似性。

下面介绍唐代中国从汉代（公元 200 多年前的秦汉）到明代（公元 15 世纪）的绘画（主要是壁画）及其技术与颜料。

西汉壁画（比公元前 210 多年前的秦汉约晚 100 多年）

1972 年出土于中国湖南长沙马王堆一号汉墓一幅大的 T 字形帛画，保存完整，是中国迄今为为止所发现的最早的完整的一幅绘画作品，同时出土的还有墓主人—尸具和许多漆器等陪葬品。

帛画帛（丝织品）出图原为白沙，现已变为黑褐色。但经 2100 多年并未破损，历史证明天然植物是持久的。

装饰性构图，画面对称、均衡、色彩华丽协调，颜色基本上使用矿物质颜料，有朱砂、石青、石绿、植物颜料有花青（蓝色）、石绿等色彩，白色是用高岭土和高岭土（氧化钙、氧化镁等）。

绘画技术，造型用墨线勾，略有渲染，不求立体。展示西汉帛画版和中国石墨石板标本图、青石—青金石、蓝铜矿、朱砂、石绿等。

中国古代 4 世纪—7 世纪的绘画，敦煌北魏、西魏、北周壁画，新疆克孜尔（古龟兹国）壁画。

敦煌位于古代丝绸之路之上，古丝绸之路是中国通过阿拉伯、欧洲诸国的重要通道。敦煌的莫高窟 400 多个洞窟壁画，是东西方文化交融的成果，其作品已融合了东西方绘画的技法。

敦煌壁画中颜料都是佛教题材，佛教本身从印度传到中国，它的绘画技法和绘画技法很自然地结合了中国和印度的双方。

敦煌壁画期（4 至 7 世纪）的洞窟壁画与印度阿旃陀壁画风格与绘画技法。有北魏、西魏、北周的壁画。其画为佛教故事画为主，亦有佛像。敦煌壁画手法自由、不拘一格，但自然形成均等。色彩强烈，颜料以矿物颜料和土质颜料为主。有朱砂、石绿（malachite）、朱红、石蓝、石绿粉、外白（白土）、黑（黑）及部分植物颜料花青、胭脂色等。但氧化铅颜料、硫化汞（银朱）等化学颜料多至白化。

克孜尔壁画，风格与绘画技法、颜料相似，是公元 7 世纪的作品，壁画以青、绿、红色为主。

敦煌莫高窟唐宋壁画（公元 7 至 12 世纪）以及唐李唐壁画（7 至 12 世纪）

唐朝 7 世纪前后的壁画，为 7 世纪，李唐画派的 influence。画家所修画，规模宏大，画室壁画精美宏，大、用色讲究。壁画大量使用矿物颜料朱砂、石青、石绿等，使画面华贵壮美。唐代画色比 7 世纪前进步，如石色已分多种色相，至作较精采。

敦煌西夏壁画，宋代的壁画（7-12 世纪）

此阶段绘画颜料已将合成化的氧化铝、硫化汞等易变色的红色、红色、朱黄色等颜料废弃不用。故壁画保留了较鲜明的色相效果，历时千多年不变色。桔红色和朱黄色用朱砂的色最细腻，用在人物面部很过烂。植物颜料花青、胭脂等用于色的打底部分。在 12 号唐代洞窟中佛像身体、面部还用了氧化钛（TiO2）。

壁画色调多用暗色调，如红、绿、黄等色，青色较少（彩图 V, 4, 3a), 而克孜尔壁画中的青绿色较多，红色色不，比敦煌色调对比强烈，绘画技术趋于精制，画面装饰性强，背景时期的较自由的，随意的构图和设色的方法。
元朝(13-14世纪)的壁画

元朝虽然为蒙古民族统治，但文化上蒙古对汉族的影响不大。从壁画方面看，永乐宫道教壁画完全保留了唐宋壁画的风格与特点。

道教是中国的传统宗教，所以神仙的造像与服装全是汉族唐朝时样式。

敦煌也有一部分元代壁画，但多用透明色，更加注意线条的美感，大约受文人画影响。

元永乐宫壁画绘画技术纯熟，三青殿气势雄浑。笔者从50年代至70年代三次去过永乐宫临摹，约6个月。后二殿为道教故事画。

三青殿颜料中有金属颜料，多为“堆金沥粉法”，即在壁画做成凸出的白粉线条，干后再在上面贴上金箔，形成金色花纹或图案，增强壁画的华美效果。

明代法海寺壁画(公元15世纪)

明代法海寺在北京西郊，为明代初皇家所建，由皇家的画师绘制壁画，费时数十年。画技精湛，颜料十分考究。几乎全部使用矿石颜料，包括加少的白云母粉(MiCa)。在云气、荷花、牡丹花、人物的面部和服饰上，水月观音的纱带背上都用细云母粉罩过或画过，形成微微闪光的效果(彩图V.3)。我从巴黎一位教授那里了解欧洲也用云母粉作画。

法海寺大量使用金箔，其技巧复杂，与同时期欧洲尼德兰画家凡·艾克在祭坛画上所用的贴金箔图案的方法相同。我在荷兰根特城见过凡·艾克的作品，不止贴金箔，他的石青、朱砂的绘制技艺十分高超。

至明朝末年，东西贸易交流更多了起来。绘画技术和颜料交流较多，属于另一研讨题目。“

Jiang Caiqin

Painting Technique in Ancient China

The author of this paper (see colour plate V), who has not only copied from frescoes in ancient Chinese Dunhuang caves and Yangle Palace but has also visited many European museums and churches, holds that ancient Chinese and Europeans were synchronous in the development of painting. There were similarities in their painting techniques and the pigments they used. This paper explains the history and characteristics of the development of ancient Chinese painting and also offers a comparison with historical European painting (till 15th century). The following two historical stages will be explained:

(1) Pigment used in China and Europe before Christ
   China: Period from Zhou to Han Dynasties
   Europe: Period of Ancient Greece and Rome

(2) The Middle Ages
   China: Period from Han to Ming Dynasties
   Europe: Period from the Middle Ages to the 17th century.
Petra Rösch

Colour Schemes on Wooden Guanyin Sculptures of the 11th to 13th Centuries, with Special Reference to the Amsterdam Guanyin and its Cut Gold-foil Application on a Polychrome Ground

Fine threads of gold-foil are a special mode of surface decoration, and up to now have been considered typical for Japanese Buddhist works of art.¹ On numerous sculptures and paintings in Japan a decoration with thinly cut gold-foil, called ‘cut gold’ (Japan: kirikane), adorns the skirts and scarfs of holy beings in the Buddhist world.

In China these geometric patterns, made from extremely thin gold threads, do not seem to have been very common and are rarely found nowadays, even though gold-foil applications, generally called ‘applied gold-foil’ (Chinese: tiejin), are known at least since the 6th century dynasty. Until now it has been assumed that this skillful surface decoration had its origins in China, but reached its highest refinement in Japan. However, because of the scarcity of known material, the circumstances of the Chinese cut gold-foil decorations have so far not been properly investigated.

With the help of new material which has become available through closer examination and the restoration of Chinese wooden sculptures of the Song, Liao and Jin dynasties in Western Museums, not only the assumption that kirikane originated from China can now be confirmed, but furthermore the close relationship between Japanese decoration techniques and their Chinese predecessors can now be established as well. As Japan offers a well-studied and adequate range of examples of kirikane, I will refer to Japanese sculptures to illuminate the Chinese development of cut gold-foil applications.

After a short introduction, I will consider some technical questions. To examine the relationship between Chinese and Japanese cut gold-foil decorations, it will be necessary to take a short look at the development of cut gold-foil in both countries. In the second part of the paper, the emphasis will be laid on the Water-Moon Guanyin, kept in the Rijksmuseum in Amsterdam, which shows a complex surface decoration with cut gold-foil.

Today, most of the wooden sculptures of the 11th, 12th and 13th centuries no longer show the original polychromy, because of more recent redecorations. Many of them have, however, preserved coats of paint which are datable to the Ming dynasty.² They now appear in an overall golden colour, with additional relief or pastiglio patterns on their skirts and scarfs. A short comparison of the front and back of the Guanyin sculpture in the Art Institute of Chicago (fig. 1) shows the different colour schemes: a completely golden surface on the front and a more colourful and varied rendering on the back (fig. 2), which probably reflects the original decoration of the 11th to 13th century.³

A similar situation can be observed on the Amsterdam Guanyin (fig. 3 and colour plate VI, 2), where the golden Ming period surface decoration was removed in the 1940s, to reveal a more realistic surface decoration underneath.⁴ Hopefully, many more original surface decorations of this period will come to light in the future through close examination and restoration of these sculptures. In any case, from what is known today we can safely assume that all sculptures of the Song to Jin dynasties—including the Amsterdam Guanyin—were originally decorated in a more ‘realistic’ and more colourful rendering.

Cut gold-foil was obviously an important component of this realistic conception. To proceed further, it is necessary at this point to focus briefly on the meaning and on some technical aspects of cut gold-foil applications.

Gold-foil was applied on Buddhist sculptures and paintings in order to give them a precious appearance. Gold itself was not seen as mere decoration, but as a gift to Buddha. Thus the decoration of Buddhist works of art with gold and silver was a way of expressing ones devotion to Buddha. Gold or silver paint was conceived as more precious than ink or paint, and in turn cut gold-foil was more precious than painted gold and thus expressed greater devotion.⁵

Gold-foil applications on sculptures most probably represent gold-thread embroidery or designs rendered in colour and gold-foil imprints on textiles. They most likely imitated not only Chinese textiles, but also those influenced by Central Asia clothes. In the future it needs to be considered how far cut gold-foil patterns did in fact refer to textiles, and where they developed their own effects, through, for example, straight lines and sharp angles.⁶

Technically, Japanese kirikane or cut gold-foil decorations need a careful preparation of the material. Three layers of thin gold-foil leaves are joined together through heating (fig. 4). Thus the foil becomes thicker and does not tear as easily. Next, a sharp bamboo knife is used to cut threads of gold-foil up to 3mm width. With glue made out of seaweed and a brush to pick them up, the gold threads are applied to a coloured surface or an unpainted wooden ground. While carefully applying the threads to the surface, the patterns, consisting of bent-lines or geometrical schemes, are developed.⁷

In the following section of the paper I will trace the development of cut gold-foil decoration in China and Japan. Cut gold-foil decorations existed in China prior to the Song dynasty, and influenced Japanese works of art. The origins of gold-foil applications on sculptures go back at least to the Northern Qi dynasty (550-577), as examples from recent excavations in Shandong province, Qingzhou, have shown.⁸

One of the earliest examples of cut gold-foil decorations representing textile patterns can be seen on the clothes of Bodhisattvas in Dunhuang. Until now, the art of cut gold-foil decorations in Dunhuang has not been analysed in detail, but recent research into patterns on the dresses of the Bodhisattvas in Dunhuang demonstrates conclusively that cut gold-foil was used in various ways from at least the Sui dynasty onward.⁹ These patterns included designs of applied cut gold-foil which are very similar to the early kirikane patterns found in Japan. In the Sui dynasty cave No. 427 hands of rhomboid patterns of cut gold-foil (fig. 5) are interspersed between fields of coloured patterns. Although these early Chinese cut gold-foil patterns do appear a bit crude, they make apparent that the technique of imitating golden textile patterns on sculptures was already well-known in China at the time.
Another Chinese example showing early Chinese cut gold-foil decorations is the marble sculpture of Da Anguo Si at Xi'an, consisting of a marble base and a Buddha, now in the Shaanxi History Museum (fig. 6). This time it is not textiles which are imitated; instead, the edges of the lotus throne are highlighted with lines of cut gold-foil, and the lotus-leaves decorated with flowers made out of tiny cut gold-foil rhomboids (fig. 7).

In the following examples it should become clear that the Chinese patterns were the inspiration for Japanese works of art, as Japanese sculptures show comparable patterns of tiny lozenge-shaped pieces of gold-foil which are combined with threads of cut gold-foil. One of the earlier gold-thread decorations still preserved today can be seen on the trousers of Bishamonten from the 9th century (colour plate VI, I) in the former Ordination Hall (J. Kudōin) at Tōdaiji Temple in Nara from the 9th century. On a green ground we see a geometric pattern of cut gold-foil threads, with flower-motives of lozenge-shaped pieces inbetween. Motif and technique are not only comparable to the Da Anguo Si marble base, but also to the patterns we have just looked at on Bodhisattvas' dress in Dunhuang. This cross-reference confirms that already at this early stage cut gold-foil patterns on Japanese sculptures were inspired by Chinese works of art. To sum up so far, the early patterns in cut gold-foil in Japan, as well as in China, consisted of simple geometric patterns of fine lines and rhomboid shapes.

For Japanese kiri-kane decorations it is generally accepted that the simpler patterns gradually developed into more complicated forms, which in this case means that simple patterns of a few lines grew into dense, net-like patterns. The development of more complicated motifs began in the 11th century, but during the 12th and 13th century the art of kiri-kane decorations had reached its peak. As the technique was by then fully understood and mastered, thin threads of gold-foil could be used more freely. From that time on, bent lines were en vogue, forming motifs like clouds or waves, and many flower and leaf patterns or complex geometric patterns appeared.10

This summit of achievement in the 12th and 13th century clearly coincides with new influences in carving styles and decorations from China. Japanese Buddhist sculptures not only bear influences from China in their carving, but also show surface decorations and patterns of cut gold-foil which are obviously influenced from China.11 The sitting Kannon (C: Guanyin) of the 12th and 13th century kept at the Senjōji Temple in Kyōto is just one example which clearly records this connection; with its grape-leaf garlands of cut gold-foil on its knees and coat, it recalls features which appear in Japan with the beginning of the Kamakura period (fig. 8). Patterns on Kaikei sculptures appear to be modern for the time and had not previously been used in Japan in this way. Kaikei is a sculptor whose style is said to have been influenced by Chinese art of the period.12 Grape-leaf design on the borders of the Kaikei's Amitabha's dress show up in a new variation during this period, as well as a complex hemp-leaf pattern, which covers, for example, wide areas of this sculptures attire (fig. 9). The complex geometric, net-like patterns and the more natural ones with complicated bent-lines had their origin in Song China, too, an observation, which will be supported by the following Chinese examples.

Fig. 1: Guanyin, 11th-13th century, front; Art Institute of Chicago (Photo: author).

Fig. 2: Guanyin, 11th-13th century, back; Art Institute of Chicago (Photo: author).
Until recently very few Chinese sculptures which could confirm the hypothesis that the patterns of 11th and 12th century decorations were influenced by Chinese sculptures have been found. The examples of Chinese sculptures to be presented next will demonstrate that the variety and complexity of Chinese cut gold-foil-patterns was more than capable of inspiring the refined patterns seen on Japanese sculptures. Due to improved photography and recent restorations, it has become possible to thoroughly document Chinese wooden sculptures with cut gold-foil decorations. The richest example in this respect is the Water-Moon-Guanyin of the Rijksmuseum in Amsterdam. Fine geometrical and bent-line patterns in complex arrangements can be appreciated on this sculpture, and with it we can gain an impression of how high-quality pieces were decorated in China during the Song to Jin dynasties.

The sculpture of the Water/Moon Guanyin in the Rijksmuseum, Amsterdam, dated to the 11th/13th centuries, was one of the first Chinese works of art on which a cut gold-foil decoration
Fig. 6: Da Anguosi-Buddha, marble; Shaanxi History Museum (Repro from: YOSHITAKA).

图6. 大安国寺-佛，大理石，陕西历史博物馆（取自：义孝有贺）。

Fig. 7: Da Anguosi-Buddha, detail of marble base; Shaanxi History Museum.

图7. 大安国寺-佛，大理石宝座局部。陕西历史博物馆。

Fig. 8. Kannon, 12th/13th century, detail of the left knee, floral spandrel decoration; Senyūji Temple, Kyōto.

图8. 观音。12/13世纪，左膝局部，蔓花装饰。京都泉涌寺。

Fig. 9. Buddha Amitābha, Shunjōdō, Tōdaiji, 1208, detail of the garment, hemp-leaf-decoration.

图9. 阿弥陀佛，东大寺，1208，外衣局部，大麻叶装饰。
Fig. 10. Guanyin, detail around the knee; Amsterdam, Rijksmuseum (Photo: Rijksmuseum).

图 10. 观音，膝处局部；阿姆斯特丹皇家博物馆(摄影: 皇家博物馆)。
comparable to Japanese examples was found (comp. fig. 3 and colour plate VI.4). The sculpture of ‘Guanyin sitting in Royal Ease’ has already been discussed by Dietrich Seckel, Heidelberg University. He praises the sculpture not only for its refined style, but especially for its well-preserved cut gold-leaf applications.  

The gold-foil-decoration on the skirt was discovered in the 1940s when the sculpture received a surface treatment. During a second investigation conducted in 1998, a more detailed picture of the paint layers could be achieved and close-up shots of the cut gold-foil decoration could be taken; these allow us now to get a clearer impression of the patterns on the skirt. The dhoti or skirt of this sculpture offers three different, complex cut gold-foil applications, all consisting of extremely thin threads of gold-foil on a bright red coloured ground.

The area of the knees (fig. 10) is separated from the rest of the skirt through five wavy lines of cut gold-foil. Here, the impression is of a net of stars covering the area. The pattern was probably developed geometrically according to a chequered board; this can be seen best in a drawing made by Eri Sayoko, one of the few kirikane masters in Japan today (fig. 11).  

A comparison makes clear that the pattern on the Amsterdam Guanyin can be described as a hemp-leaf pattern, very much comparable to the Japanese examples discussed above.

But the Amsterdam Guanyin is not the only Chinese sculpture with such an application known today. This kind of cut gold-foil pattern was obviously quite common in China. It can be seen too, for example, on the sleeves of a sculpture of Weiwo Tian, the protector of relics and books (colour plate VI.3). This sculpture, dated to the Southern Song dynasty (1127-1278), is kept today in Choryuji Temple in Gifu province. It is generally accepted that it was brought there from China in the 12th century. In another variation, the hemp-leaf pattern is interspersed with small cross-shaped flowers.

Another sculpture, also dating to the 12th century or earlier, also comes from the southern part of China. In the Provincial Museum at Hangzhou a little clay sculpture, about 40-50 cm high, is on display. It can be roughly dated to the 10th to 12th century and is assumed to come from Baixiangta Pagoda, west

Fig. 11. Geometrical pattern development (Repro from: Yoshitaka).

图11. 几何图案发展示例（取自：义孝有贺）
of Wenzhou City, in the southern part of Zhejiang province (fig. 12). In its lap, on a red coloured ground, it shows a hemp-leaf cut gold-foil pattern, very much comparable to the one we’ve encountered on the Amsterdam Guanyin (fig. 13).

The above-mentioned three examples of hemp-leaf pattern clearly show that this kind of cut gold-foil pattern was prolific in China from at least the 12th century onwards.

The largest area of the skirt of the Amsterdam Guanyin is covered by a net-like pattern of connected hexagonal shapes (fig. 14 and colourplate VI.4). Again, this is a pattern quite common on Japanese sculptures since the early Kamakura period (colourplate VI.5). An interesting fact worth noting here is that the hexagonal pattern on the Amsterdam Guanyin’s skirt is obviously not only just laid over the red coloured ground. It would appear as well that the green clouds and phoenixes or cranes, which also decorate the skirt, are covered by the cut gold-foil pattern too. This seems unusual in comparison with Japanese examples, which always differentiate clearly between polychrome patterns and a cut gold-foil decoration on the ground layer. As could first be stated as a result of a recent analysis by Aleth Lorne, the cut gold-foil decoration of the Amsterdam Guanyin could also be a later over-decoration, applied after the first coating of a red ground colour with interspersed clouds and phoenixes.16

Another pattern belonging to the Amsterdam Guanyin’s cut gold-foil decoration can be seen on a wide band or border along the edge of the skirt (fig. 15). As far as one can judge from the detail photograph, it consists of spade-like leaves set one beside the other. The pattern seems not to be one of any geometric consistency, but made instead of freely-set, bent or curved lines. The distribution of lines is not very dense, standing rather in the tradition of naturally distributed grape-leaf garlands known from Japanese sculptures at the beginning of the Kamakura period, like the above mentioned Buddha Amitābha from Kaikei or the Kannon from Senyūji temple.

Non geometrical, bent-line patterns do not only turn up on the Amsterdam Guanyin, but also on other Chinese sculptures datable to the 12th century and earlier. On the already mentioned Weituo Tian, for example, we find next to the hemp-leaf pattern a decoration of wave or cloud-like cut gold-foil application (comp. colourplate VI.3). Furthermore, I would like to consider the small sculpture sitting in ‘royal-case’ which came up for sale in the Eskenazy summer exhibition of 1990 and was published in the catalogue (fig. 16 and 17): as can be deduced from the detail, while the arrangement of single threads of gold-foil is like an arm of a hemp-leaf-pattern, the lines next to it suggest that this was part of a more complex motif, perhaps flowers, as can be seen on the coat of Amida’s dress. That flower and leaf motifs out of cut gold-leaf were used on Chinese sculptures as well is demonstrated in a further example. On the skirt of a nearly lifesize sculpture of a sitting Guanyin cut gold-foil decoration has come to light under a Ming dynasty coating (fig. 18). The piece was exhibited in a Deydier sales exhibition in 1996 and is now in a private collection in Taiwan. The detail (fig. 19) clearly shows the naturally rendered leaves of a flower, belonging to a pattern which obviously covered a larger part of the skirt, as the pattern seems to continue adjacent to the flower. The distribution of flower leaves even seems comparable to the grape-leaf pattern shown already on the Japanese sculpture of Chōryūji in Gifu province, where flowers were organized in a border-like band.

From what we have seen of Chinese cut gold-foil decorations on the Amsterdam Guanyin and on other examples it is obvious that complex net-like and geometric patterns as well as bent-line, flower-leaf patterns were firmly established by the 12th century and could thus have influenced the Japanese Kamakura patterns. The covering of the dresses with a system of cut gold-foil patterns, as could be observed on the skirt of the Amsterdam Guanyin, is also very similar to Japanese examples.

In conclusion cut gold-foil decoration had its origin in China and influenced the Japanese patterns at least twice, in the 7th/8th centuries and in the late 12th/13th centuries. Decorations with complex patterns of cut gold-foil were no isolated phenomenon, but frequently employed on Chinese sculptures in a highly
Fig. 13. Sitting Guanyin, 10th/12th century; detail of the skirt; Hangzhou Province Museum.

图 13. 坐观世音，10/12 世纪；裙子局部；杭州浙江省博物馆。
skilled manner. The cut gold-foil designs discovered on Chinese sculptures during recent years are in quality and variation comparable to Japanese pieces. Further research and technical examination of sculptures kept in the collections of museums or still in situ in Chinese temples will be necessary in order to support and develop these observations.

Notes

3 At the moment the sculpture is under examination by the Art Institute's Conservator.
8 WENWU 1998, 2, pp. 4-20.
9 ARIGA 1997, p. 23, plate 69; CHANG SHAN: Dunhuang Lidai fushi tu'an (Dress Patterns in Dunhuang through the Dynasties), Hong Kong 1986, p. 8.
10 SIECKEL 1954, pp. 82-85.
14 ARIGA 1997, p. 91.
15 ARIGA 1997, p. 68.

Fig. 18. Deydier Guanyin.

Fig. 19. Deydier Guanyin, detail of the skirt.

Fig. 19. Deydier Guanyin,裙子局部。
11 至 13 世纪木制观音像的彩绘结构:
以阿斯特丹观音及其金箔在彩绘表面上的应用为重点

宋、金、辽雕塑的装饰问题，我想在我的博士论文中进行探讨。这里我想重点讨论在西方博物馆收藏的结跏趺坐的自在观音木雕像。

关于宋、金、辽时期雕塑彩绘的研究不多。重要的出版物有约翰·拉森和罗斯·克尔编著的保护报告“观音 - 展示一件杰作”(伦敦，1985 年)，作者关注的是维多利亚和艾伯特博物馆的雕塑。除此之外，只有极少的且大多没有发表的在西方博物馆所做的观察工作。

佛教雕塑是宗教环境的组成部分，受时尚的影响，它们中的大多数都重复修过多次。原始表面常常被重新覆盖在全然不同的表面之下。随着研究方法的改进，愈来愈多的雕塑彩绘结构的真相暴露出来，引人入胜的细节得到揭示，这些为了解彩绘概念提供了新的线索。

我在报告中着重介绍 3 座在西方博物馆收藏的结跏趺坐的自在观音木雕像，它们分别藏在维多利亚和艾伯特博物馆、芝加哥艺术学院和阿姆斯特丹皇家博物馆。

在仔细观察这几件雕刻时，我讨论和分析了其彩绘，特别是一些阿姆斯特丹的观音像的切金装饰。

我将围绕下列几点对这些雕刻进行探讨：
- 新修装饰阶段的全部金色覆盖层。
- 3 座雕像的围巾、披巾和罩裙上的彩绘。
- 阿姆斯特丹的观音像上的切金装饰。

初步结果：所有有金色装饰的 3 件雕刻的技法类似，均以“压地隐起”之法pastegiato构成浮雕花卉图案。覆盖层可能是辽代之后产物，看来反映了不同的宗教雕塑思想。
- 原始彩绘结构大多受到纺织品的启示。阿姆斯特丹的观音像的装饰看来最为先进。
- 在阿姆斯特丹的观音裙上看到的切金装饰也许并不象迄今所想象得那么独特，一大批宋至辽代雕塑的图案影响了日本平安和镰仓时代的木雕。

这项研究的目的在于更好地理解彩绘的发展，获得更好的断代方法，确定这些雕刻在中国艺术史中的地位。

(英文译：陈钢林)
Sylvie Colinart and Sandrine Pagès-Camagna

Egyptian Polychromy: Pigments of the “Pharaonic Palette”

Introduction

Paint was widely used in Ancient Egypt for the decoration of both large-scale monuments and small objects. Colour performed a complex function here: it imitated nature, but it also conveyed symbolic meanings. The pigments of the “Pharaonic palette” consisted mainly of natural minerals whose ores were widespread in Ancient Egypt (Colinart, et al., 1996).

There is ample literature on the subject, but Lucas’s Ancient Egyptian Materials and Industries, first published in 1922, remains the starting point for most research in this field (Lucas, 1962). Data going beyond Lucas can be obtained by systematic scientific investigation of polychromed objects. The Research Laboratory of the Museums of France (LRMF) therefore performed tests on selected monuments and artefacts in the Department of Egyptian Antiquities (DAE) at the Louvre with a view to identifying the chemical constituents of various colours and determining the processes by which they were made.

The tests were carried out using a set of techniques, including optical microscopy, scanning electron microscopy coupled with an X-ray analysis system (SEM-EDXS), Raman microscopy and X-ray diffraction. Materials were investigated in the form either of small chips taken from the objects or of samples produced in accordance with experimental recipes. The samples were embedded in resin in order to facilitate observation and analysis of their cross-sections. The results presented here focus on the yellow colour (Colinart 2001) and on a green copper silicate synthetic pigment known as Egyptian green.

Yellow

For the Ancient Egyptians, yellow derived from the sun and therefore signified life and growth. In their painting, they used it to depict vegetal materials, some foods and women’s flesh. Tests performed on yellow polychromy revealed the materials traditionally employed in this context and mentioned in the literature: gold, orpiment, umber and iron oxides.

Traces of gold were found on the face of a painted sandstone image of the goddess Satis from the chapel Elephantine, which dates from the reign of Thutmose III (1479–1425BC, Louvre, B69), and on coffins. In the latter case, the sheets of gold either covered the entire coffin (coffin of King Antef, 17th dynasty, 1650–1550BC, Louvre, E3019/N712) or were found only in flesh areas or in certain ornaments (coffin of Mesre, 18th dynasty, Louvre, N2673; coffin of Tamoutnofret, late New Kingdom, 1186–1069BC, Louvre, N2571). Gold, easily obtainable in Ancient Egypt, was used because of its symbolic, not its material value. Associated with immortality, it was employed to represent the flesh of Re and all other divine beings. It was thought to assist the dead in speaking and eating in the afterlife. Such powers were also attributed to orpiment and sometimes to yellow pigment.

Owing to its bright yellow colour, orpiment could be used as a gold substitute symbolizing Re’s spirit. A natural arsenic sulphide, As₂S₃, it is more intense in colour than ochre or iron oxides. Its use in the Middle Kingdom (2033–1710BC) is attested, but we found it on the 2nd dynasty (2900–2700BC) stone stela of Nytoaa and Nytnof from Saqqara where it would seem to belong to the original polychromy (Louvre, E27157).

The pigments encountered most often on polychromed objects from our period of study were ochres and iron oxides, the most widespread in the world. These natural minerals were found in flesh areas, in the backgrounds of hieroglyphs and in many decorative patterns. The composition of materials generally termed “ochres” has not always been defined precisely. They usually consist of clay with variable amounts of such iron oxides as goethite (α-FeO·OH) and limonite (Fe₂O₃·H₂O).

Our analyses revealed some less familiar minerals among the yellow pigments. These anhydrous hydroxyl iron sulphates belong to the jarosite group of minerals (Colinart, 1998), which in turn form part of the alunite group. Their colour varies from light to brownish yellow. The best known among them, encountered on some objects, are the yellow components jarosite, KFe₃(SO₄)₂(OH)₆, identified by Le Fur in Middle Kingdom pigments in Karnak (Le Fur, 1994), and natarojarosite, NaFe₃(SO₄)₂(OH)₆. Ornaments painted with these pigments show layers more lemon in colour and with more crystallization than in pigments made from ochre, iron oxides or orpiment (colour plate VII, fig. 1). An example is found in the mastaba of Akhetetep from Saqqara (5th dynasty, 2500–2350BC, Louvre, E10958; colour plate VII, fig. 2). Backscattered electron images of sample cross-sections reveal the morphology of these minerals. Frequently cubic or hexagonal, they are of medium size, generally 2 to 6 micrometres, but sometimes reaching 15 or 20 micrometres (colour plate VII, fig. 3). Scanning electronic microscopy analysis indicates that the composition of these sulphates is more complex than that of jarosite and natarojarosite. Their SEM-EDXS spectra show the presence of much sulphur and iron, associated with potassium in jarosite and with sodium in natarojarosite. Substitution of sodium by potassium gives rise to intermediary components. The proportion of these two alkali elements can vary within a single mineral grain or layer of paint, as was found in the yellow used on the mastaba of Akhetetep. Another phenomenon may be observed on the coffin of Henem from Asyut (Middle Kingdom, Louvre, AF9757): the partial substitution of iron by aluminium, giving the mineral a different hue. The yellow decoration inside the coffin contains little aluminium, whereas that outside shows approximately 50% of the iron substituted by aluminium, producing a whiting tone.

This jarosite group of minerals was identified on artefacts dating from the Old Kingdom (2700–2200BC) to the Ptolemaic period (332–30BC) and on the later Fayyum portraits. They reportedly occur in nature as a result of alterations in iron oxides or pyrite caused by dry climatic conditions (Wallert, 1995), the
type of iron sulphate produced depending on the geological context. Another opinion, based on research into the deterioration patterns of pigments found on Ancient Egyptian monuments, explains the presence of jarosite as resulting from the advanced decomposition of an iron-bearing glass pigment containing potassium and sulphur (Schiegl et al., 1992). According to this view, the result would be complete substitution of the glass pigment and a green or red-brown colour.

Samples examined in the LRMF showed no traces of characteristic marker elements from iron-bearing glass pigments. The thickness of the yellow layers averages 20 to 50 micrometres. The backscattered electron images often reveal sulphate grains with a disorganized orientation, which proves their natural origin. For most of these yellow minerals, associations of potassium, sodium and aluminium would seem to provide an additional criterion of natural origin.

Our investigations also showed that painters used these minerals in conjunction with other yellow pigments on one and the same object, including the coffin of Henem. Some motifs leave no doubt that the colour intended was yellow. The drapery of Neferetabet in the eponymous relief from Giza, for instance, is clearly meant to be made from panther's fur (4th dynasty, 2620–2500 BC, Louvre, E15591).

Our tests, made on nearly 40 objects from the DAE, confirm that the presence of minerals from the jarosite group resulted from decisions made by Ancient Egyptian craftsmen to paint certain areas yellow. However, those tests do not permit us to exclude entirely the possibility that jarosite may have been produced by the alteration of iron-bearing glass pigments.

**Egyptian Green**

In addition to natural minerals the Ancient Egyptians made synthetic pigments. The best known of these pigments is Egyptian blue, similar in structure to the Han blue found on the soldiers of the terracotta army (Wiedemann, 1998). With the exception of cobalt blue – another synthetic product, discovered on some painted ceramics from the 18th dynasty (Noll, 1981) – Egyptian blue was used for all blue decoration. The first such pigment is thought to have been made in Egypt itself, where it is found from the 4th dynasty through to the Roman period. It was in use throughout the Mediterranean area until the 7th century AD. Thereafter, knowledge of the recipe seems to have been lost. No Egyptian sources describe the process, but Latin recipes are recorded by Vitruvius, Pliny the Elder and Theophrastus. Following the discovery of Egyptian blue in the wall paintings at Pompeii, the first attempts to investigate Egyptian blue recipes were made in the 19th century.

The Egyptians also made a light green synthetic pigment, less well known than Egyptian blue and less frequently analysed (colour plate VII, fig. 4). This pigment, used as a substitute for turquoise colour and identified in the second half of the 20th century, has the same constituents as Egyptian blue – silicon, calcium and copper – and has been given an analogous name: Egyptian green. No recipe has been found or suggested, not even in Antiquity.

The first hypothesis offered to explain the origins of Egyptian green was that a chemical process used to make Egyptian blue failed, producing instead a green colour owing to the unexpec-
The presence of iron in the raw materials, to mixing the ingredients in incorrect proportions or to the firing conditions. Egyptian green has also been seen as an intermediary product obtained during the making of Egyptian blue and as the result of alterations in Egyptian blue itself (Schiegl et al., 1989). The latter theory has not withstood analysis, which showed that the alteration products were copper chloride or copper carbonate, neither of which occurs in Egyptian green. In fact, there is no evidence that Egyptian green resulted from a physical transformation of Egyptian blue. Moreover, the presence of both pigments on one and the same object but in different patterns indicates that both were used deliberately for distinct iconographical purposes.

Despite this evidence, Egyptian green is still generally held to be a derivative of Egyptian blue. Indeed, the two copper silicate pigments are frequently confused with one another and with the items of faience and glass named after their colour. It was thus essential to eliminate all misunderstandings about these various copper-coloured materials.

Analysis of ancient pigments from the DAEE collection of samples, and our own specially made pigments, enabled us to define the physico-chemical properties and their relation to each other. In order to understand better how they were produced, experimental recipes were prepared in the LRME consisting of a mixture of calcium carbonate, copper oxide, pure silicated sand and sodium carbonate, heated together (Pagès-Camagna, 1999). The powders were ground and mixed together with a little water. Structural analyses of green and blue archaeological samples and of our experimental samples revealed the great complexity of the materials after sintering. In fact, they appear to be composites, the result of a mixture of amorphous and crystalline phases:

- Egyptian blue is characterised by the presence of cuprorivait (CaCuSi₅O₁₄), a blue tabular crystal, firing residues such as silica (quartz and/or tridymite) and an amorphous silicate phase. The blue sample absorption spectrum shows two thin bands at 12800 and 16200 cm⁻¹ and a shoulder at 18800 cm⁻¹. The colour of Egyptian blue derives from the presence of Cu²⁺ in a square-plane environment in the crystalline cuprorivait. It results from a mixture of compounds containing copper, calcium, silica and 1% flux around the cuprorivait stoichiometry, sintered in an oxidizing atmosphere at a temperature of 850–1100°C.

- Heating different amounts of the same compounds – more calcium and flux, less copper – at 950–1150°C under the same atmospheric conditions produces Egyptian green. It contains a copper-bearing paravollastonite (CaSiO₃) with 2% copper, residual silica (quartz and/or tridymite or cristobalite) and firing residues, embedded in a silicated amorphous phase. At 950°C and with up to 7% flux, tridymite replaces quartz. Cristobalite appears at higher levels. Tridymite and cristobalite never exist together. The amorphous phase induces a green absorption spectrum completely different from the blue one. The green spectrum has a unique broad band that reaches its maximum width at approximately 12000 cm⁻¹. This is consistent with the absorption spectrum of Cu²⁺ in an octahedral environment in an amorphous phase (fig. 1).
The firing residues of both pigments included metallic elements, among them tin and lead, indicating that metallurgists and pigment-makers worked together. This also means that, with Egyptian green, X-ray diffraction, TEM and Raman microscopy revealed no visible deformation of the crystalline structure owing to the presence of copper in the parawollastonite (fig. 2), unlike with iron-bearing wollastonites.

Our research thus shows that, although Egyptian blue and Egyptian green are provided from the same components and are produced in very similar conditions, each is made by its own distinct process.

Summary

The Research Laboratory of the Museums of France examined polyvalent objects in the Department of Egyptian Antiquities at the Louvre using such techniques as optical microscopy, scanning electron microscopy coupled with an X-ray analysis system (SEM-EDXS), Raman microscopy and X-ray diffraction. This article presents new findings with regard to yellow and to the green synthetic pigment known as Egyptian green. They show that new data is still obtainable and that Lucas's standard work on the subject is in need of revision.

References


科利纳·帕热斯·卡马那

埃及的彩绘：法老调色板上的颜料

摘要

绘画材料在古代埃及艺术中得到了广泛的应用，大量的粘性性作品和博物馆收藏的小型艺术品上都可看到它们的痕迹。色彩本身所起的作用很复杂：它模仿自然，也用于突出具有象征意味的所绘对象的特殊含义。

法老调色板上的颜料大多取自于大自然中的矿石，这些矿石遍布古代埃及地区(科利纳等，1996年)。

绘画材料方面的文献十分丰富，卢卡斯的《古代埃及材料》(卢卡斯等，1962年)是我们大多数人使用的参考书。不过由于对彩绘制品并不断的系统研究，我们始终能获得新资料。法国博物馆研究实验室(LRMP)对一些彩绘的大规模性作品和人工制品(木器、石刻浮雕和雕像)进行了研究，这些材料保存在卢浮宫埃及艺术部(DAE)

这些研究实验系借助于一系列分析手段完成的。其中包括光学显微镜、连接X光分析系统的扫描电子显微镜(SEM-EDXS)、拉曼光显微镜和X光衍射。这些研究的目的在于精确单色的不同化学成分，弄清一些颜料的生产过程。

这里主要介绍的是对黄色和绿色合成颜料即埃及绿的新的认识。

除传统的黄色颜料如金粉、氧化铁和雌黄之外，我们揭示出一组材料，这些材料作为颜料鲜为人知：即混有无水碳酸硫铁酸的黄钾铁矾(科利纳，1988年)。这些矿石在不同地区的石质制品和一些木制上发现的，时间上均沿着法老的年代顺序(公元前2700-2200)。

用这些颜料所绘的装饰表为黄色层，看来似覆有晶状物，与其说是珍珠和氧化铁色，毋宁说是用的柠檬色。我们的研究表明，它们的出现不是含铁玻璃颜料的变化，而是使用了自然的地下矿石，是由于它们不同的色彩才用的。

除了自然的矿石之外，古代埃及还合成了新颜料作为颜料：它们中最著名的乃是埃及蓝，整个古代地中海流域的古埃及蓝。这种颜料的特色是它含有硫化铜铝(Cu₂SiO₄·oH₂O)。另一方面，还使用了一种过去所知的绿色合成颜料，它通常与埃及蓝混用，埃及绿通常被看作自然降解或不成功的蓝。我们的研究显示了埃及绿有它自己的生产过程：加热与埃及蓝相同的化合物，只不过比例不同，在氧化的环境下加热至几乎相同的温度范围，与埃及蓝相似，这是一种被合成的复杂产品，是变形阶段和结晶体与混合了2%氧化的b-硅酸钻的混合物。后一种材料代表了埃及绿的特色(帕热斯·卡马那，1999年)。

这项研究工作揭示了埃及艺术家的调色板，为我们了解颜色的意义和艺术工艺史提供了新的认识。

(英译中：陈钢林)
Le Jupiter olympien and the Rediscovery of Polychromy in Antique Sculpture: Quatremère de Quincy between Empirical Research and Aesthetic Ideals

In an article published in 1827 in the New Monthly Magazine Stendhal, later to achieve fame with his novel Le Rouge et le noir: reported on a meeting of the Académie des Inscriptions et Belles Lettres. At one point he remarks that 'le grand M. Quatremère de Quincy fit son apparition. C’est le plus ennuyeux de tous les membres de l’Institut.' This low opinion of the archaeologist and art theorist no doubt resulted from Quatremère de Quincy’s championing of the Classicists in their often heated aesthetic dispute with the Romantics, a cause to which he was able to lend powerful support as an important official of the Académie des Beaux-Arts. Pace Stendhal, Quatremère is among the most interesting and original archaeologists of his time, not least by reason of his pioneering research of the polychromy of Antique sculpture, in particular that of Ancient Greece.

Born into a respected merchant family in Paris in 1755, Quatremère studied sculpture in Guillaume Coustou’s Paris studio, but broke off his training when the death of his mother in 1776 left him in the fortunate position of receiving a small pension. This enabled Quatremère to visit Rome to study the sculpture of Antiquity (colour plate VII, fig. 1). He did not return to France until 1785. The following year a tract he had written on the influence of Egyptian art on that of Ancient Greece won him the Prix de Caylus and, during the first years of the Revolution, he was appointed to a number of influential political posts due to his energetic support in the battle for artists’ rights. In 1794, however, he was denounced and arrested, yet, after being created a member of the Académie des Inscriptions et Belles Lettres in 1804, he re-entered the public arena as a loyal follower of the monarchy during Napoleon’s Hundred Days rule in 1814–15. Undaunted with offices and honours, Quatremère became Royal Censor, a member of the Legion of Honour, Inspector of Public Arts and Monuments, a member of the Conseil Honoraire des Musées près de la Maison du Roi, editor of the Journal des Savants, Professor of Archaeology at the Bibliothèque du Roi and, for the second time, Deputy for the Département of Paris. His most important post, however, was that of Permanent Secretary of the Académie des Beaux-Arts in Paris, a position he held without interruption from 1816 to 1839 (fig. 1). This key office made Quatremère the most influential and the most hated cultural personality in France, for it enabled him, a pugnacious archaeologist and Classicist, to control artistic activity in the country for over two decades.

Quatremère’s significance in the present context is as the author of Le Jupiter olympien, ou l’Art de la sculpture antique considéré sous un nouveau point de vue (The Olympic Jupiter, or The Art of Antique Sculpture Considered from a New Point of View), which he published in 1815 and dedicated to Napoleon as the Emperor’s ‘very humble and loyal subject’. This volume, its title concealing almost as much as it reveals, contains nothing less than the first history of polychromy in Antique sculpture, with the emphasis, natural at the time, on Greece. Discussions of colour in Antiquity rarely fail to mention Le Jupiter olympien, so it comes as something of a surprise to discover that its methodology and place in the historiography of the subject have never been studied in detail.

In Les Mois et les choses: Une Archéologie des sciences humaines (The Order of Things: An Archaeology of Human Sciences) the historian and philosopher Michel Foucault used disciplines as various as biology, linguistics and economics to draw attention to a rupture in the intellectual life of the eighteenth century. Caused by a lack of confidence in the possibilities of pure knowledge and the feasibility of depicting the world in linguistic terms, this rupture gave rise to two different movements - positivism, a continuation of eighteenth-century empiricism in a more radical form, and idealism, an attempt to revive metaphysical interpretations of the world. Quatremère’s position between these two poles is ambiguous, the result of his own role as both an archaeologist and a theorist.
His history of coloured Antique sculpture, the product of over thirty years' work, represented an attempt to enrich Classical archaeology by an entirely new topic of study, which, in turn, would revolutionize the discipline as a whole. It thus formed part of a wave of new sciences and specialist subjects that began in the second half of the eighteenth century and continued into the first decades of the nineteenth. Archaeology itself had been given an impressive foundation by Johann Joachim Winckelmann's *Geschichte der Kunst des Alterthums* (History of the Art of Antiquity) of 1764, which tried to place the study of Antique art on a scientific footing. Quatremère noted in *Le Jupiter olympien* that, together with the Antique works of art that he himself had seen in Rome and Naples, it was Winckelmann's writings that had awakened his passion for the sculpture of Antiquity and he had paid tribute to the German's importance as the founder of modern archaeology: 'Winckelmann donna une grande impulsion à l'étude de l'antiquité...par la seule conception synthétique de son ouvrage'. Quatremère, too, aimed at a 'synthetic conception', a study that united countless individual observations in a single overall picture. If he wished to equal Winckelmann's achievement he would need to modify, even reconstruct, both the latter's findings and the work of Winckelmann's French counterpart, the Comte de Caylus, to whom Quatremère, as a recipient of the prestigious *Prix de Caylus*, indirectly owed his academic career.

The present-day reader will be surprised by the programmatically single-mindedness and confidence with which Quatremère set about re-inventing the discipline of Classical archaeology. To use the terminology of the philosopher of science Thomas S. Kuhn, he sought deliberately to introduce a shift of paradigms, an approach that can be studied in exemplary fashion in his work. Kuhn showed that crises occur again and again in 'normal' science, which is defined by certain paradigms and exhausts itself in the 'determination of significant facts, matching of facts with theory, and articulation of theory'. Inexplicable anomalies lead to uncertainty in a discipline and to the need for new explanatory models. These cannot gain acceptance among specialists, however, until they have been promoted to the extent that new paradigms are created. In Quatremère's day and field the unsettling anomalies were Antique sculptures that showed traces of colouring and that were made of materials of various colours, for they did not accord with the accepted view that sculpture in Antiquity had been monochrome. Propagation and establishment of the new paradigm necessarily entailed the downfall of the proponents of current orthodoxy. In his work of 1815 Quatremère did not hesitate, therefore, to follow his praise of Winckelmann by excusing the German's failings: 'Winckelmann n'avait pu embrasser, ni peut-être souponner tous les points de sa circonférence.' Quatremère then delivers the crushing blow: 'le nouveau historiographe de l'art antique [i.e. Winckelmann] n'avait pas pénétré fort avant de la connaissance des divisions que comporta jadis le domaine de la sculpture...il n'avait jété qu'un coup d'œil incertain, et répandu que de faibles lumières sur ce qui constituait les diverses manières, les différentes sortes de travail des productions de l'art, les diversités de goût, d'effet, de composition, et de génie propres à chaque genre d'ouvrage.'

Quatremère's criticism was not without justification. In *Geschichte des Alterthums* Winckelmann mentions Greek clay figures that were painted red and figures that were partly gilded; sculptures made of gold and ivory or constructed from wood for the torso and marble for the head, hands and feet; figures that were clothed and, finally, a statue of Diana found at Herculanum that had painted hair and garments. Yet he either dated these pieces to the early period of Greek sculpture or simply declared them to be exceptions that proved the monochromatic rule, thus failing to recognize their true significance. For him and his contemporaries, sculptures of white marble were both the rule and the ideal in mature Greek art, for, as Winckelmann argued in his characteristically sensuous vein: 'Da nun die weisse Farbe diejenige ist, welche die meisten Lichtstrahlen zurückschickt, folglich sich empfindlicher macht, so wird auch ein schöner Körper desto schöner sein, je weisser er ist.' In *Mémoires de l'Académie des Inscriptions et Belles Lettres et Recueil des Antiquités* the Comte de Caylus, who was important to Winckelmann by reason of his comparative approach to Antique art, also mentioned sculptures bearing remains of polychromy or made of different-coloured materials, but he considered these pieces peripheral and, even more strongly than Winckelmann, rejected them as aberrations of Antique taste. Of the statue of the Parthenon Athena, which has survived in literary descriptions only, Caylus writes: 'Cette statue de Minerve présente encore une difficulté, elle était d'or et d'yvoire, et elle avait à ses pieds un serpent et un sphinx de bronze. Quel alliage de couleurs et de matières!' Behind this rejection of coloured Antique sculpture lay the Neoclassical theory of art, which enjoyed general acceptance at the time. According to this view, a strict division existed between sculpture and painting: the former was defined by form, which, like the 'dessin', the drawing or line in painting, was alone capable of reflecting the genius involved in the act of creation and, above all, the idea of a work of art. Fully conscious of these attitudes, Quatremère presented himself as the bringer of enlightenment who would overturn ideas and scholarship based on prejudice. Confidently, he wrote: 'Je me flatte...à étendre ce nouveau domaine de l'antiquité, et à détruire des préventions dont quelques-unes me paraissent avoir leur source dans le défaut absolu d'observation, et dans l'ignorance même des faits.' As a dispassionate observer, Quatremère found the causes of this ignorance not only in the Neoclassical theory of art, but also in contemporary artistic practice: not only did polychrome Antique sculpture contradict orthodox opinion; sculptors of his own day created works only in white marble and thus set the seal on aesthetic convention. This prevented archaeologists, strongly influenced by artistic theory and practice, from recognizing that Antique sculpture had been coloured: 'Car...la connaissance [de l'art polychrome] n'a manqué jusqu'ici à l'histoire de l'antiquité, que parce que les artistes n'ont jamais dirigés par la pratique de la sculpture moderne, vers la recherche de l'art des assemblages ou les ouvrages à compartiment.' Quatremère here voices the relativist opinion, astonishing for the time, that thinking is determined by experience gained during a particular time.

It was this very knowledge of historical determinants that enabled Quatremère to break through the vicious circle of theory and artistic practice. Exaggerating, one might even claim that it was only the type of historical consciousness developed in the aftermath of the Enlightenment and the French Revolution that permitted the phenomenon of coloured Antique sculpture to be accepted and appreciated. A crucial part of this consciousness consisted in recognizing the difference between one's own times and Antiquity. Quatremère expresses this with exceptional clarity when he says 'le monde ancien...venait se mettre en parallèle avec le monde moderne' or speaks of the 'vite immense, que le temps et la destruction ont laissé entre les anciens et nous'.
This historical awareness of difference culminates in Quatremère's much quoted saying (which is often misunderstood as pure empiricism): 'Il faut se persuader que les anciens employèrent les arts tout autrement que les modernes.'22 Antique art was so different because, Quatremère held, it came to being in a different social context. Hence, art can be understood, and should be judged, only with reference to its time and to the other conditions under which it arose: 'On doit donc...pour bien juger, rapprocher l'espèce de goût qui fut particulier à ces ouvrages, du genre des causes qui les produisirent et des effets qu'on en exigeait. Il ne faut pas isoler les monuments des opinions, des sentiments, des affections avec lesquels ils étaient nés.'23 These thoughts lead to a statement that would seem to anticipate the tenets of the famous nineteenth-century German historian Leopold von Ranke: 'Il faut...juger seulement en elles-mêmes, des choses.'24

This remarkably dispassionate, historical view of Antiquity had its roots in France in the ‘querelle des anciens et modernes’ (dispute between the Ancients and the Moderns) sparked off during a session of the Académie Française on 27 January 1687 by a poem of Charles Perrault's in which, contending that the age of Louis XIV equalled that of Emperor Augustus of Rome, he wrote: '[Les anciens] sont grands, il est vrai, mais hommes comme nous.'25 In its early eighteenth-century continuation as a quarrel between Homer's admirers and detractors, this dispute finally led to the ‘historicization’ of both Antique and contemporary literature and to a ‘relativization’ of both Antique and modern models.26 These attitudes inform the second part of Winckelmann's Geschichte der Kunst des Alterthums, in which the history of art is connected with historical and political events to produce a survey of the familiar growth-flowering-decay type,27 a cyclical biological model to which Quatremère also remained true. Quatremère could scarcely have adopted such a detached view of history, however, had he not experienced at first hand, as a participant in the French Revolution, the speed with which the world can adapt to altered political and social circumstances.

Returning to the subject of polychromy, we note that three inexplicable anomalies gave rise to Quatremère's revolutionary revision of notions of Antique art: references to coloured sculpture by the Ancient writers Pausanias and Pliny the Elder; reports by travellers of new discoveries in Athens; and the observations that Quatremère himself had made at the excavations of Herculaneum and Pompeii, in various Italian museums, particularly in Rome, and in the Musée Napoléon (now the Louvre) in Paris.28 It was above all Pausanias' mention of lost chryselephantine cult statues by Phidias that aroused Quatremère's interest, awakening in him a desire to explore the phenomenon of polychrome sculpture. Aware that, in order to achieve success as the brilliant founder of a science, as a 'second Winckelmann', he would need to appear as a discoverer, Quatremère placed himself in the best possible light in Le Jupiter olympien: 'En me représentant ces
grands ouvrages de l’art, la haute célébrité dont ils jouirent, la rénommé de leurs auteurs, je fus de plus en plus frappé, et du silence des critiques modernes sur une si noble partie de l’art antique.  

Antique mentions of lost cult images were complemented by first reports of remains of colouring found on sculptures from the Parthenon and the ‘Theseion’ in Athens. Quatremère, who never visited Greece, was in contact with the collector Choiseul-Gouffier, the engineer Fougerot and the French ambassador in Athens, Fauvel, all of whom had assisted in the removal of the Elgin Marbles from the Parthenon in the early years of the century and told Quatremère on several occasions that the sculptures bore traces of colour (figs. 2, 3). Further support for the idea that the sculptural decoration of the Parthenon had originally been coloured was provided in The Antiquities of Athens (1787) by the Englishman James Stuart and Nicholas Revett, who drew attention to the many holes drilled in the sculptures for the attachment of metal reins and various attributes. These, Quatremère felt, confirmed that the traces of colouring were original. From his informants’ observations on the polychromy of the Parthenon sculptures he concluded: ‘Sans être ce qu’on peut appeler peinture...elle [la sculpture] avait des parties teintées dans différentes manières, qui tantôt la détachaient du fond sur lequel les couleurs étaient appliquées, tantôt indiquaient les plans des figures par les différents tons, soit des draperies, soit de beaucoup d’autres détails.’ In Paris Quatremère could acquire for himself possible confirmation that the sculptures had been coloured, for the Musée Napoléon possessed a fragment from the Parthenon frieze. Since the significance of traces of colour was not recognized, they would have been removed during the customary cleaning, yet Quatremère vaguely remembered having seen such traces when the piece was still in the crate in which it had been transported from Athens. Further evidence of Antique polychromy was provided in 1811 and 1812 by the archaeologists Johan David Åkerblad and ‘Eduardo’ Dondwell, who reported remains of colouring on the ‘Theseion’ in Athens.

Not relying solely on the polychromy of sculpture from prominent Athenian temples, Quatremère listed all pieces known to him that bore traces of paint, the discoveries made in Herculaneum and Pompeii being particularly welcome in this respect. References to coloured sculpture in the writings of Antiquity completed his material. Quatremère proceeded similarly in the case of polyolithic sculpture and of coloured bronze pieces, amassing an impressive amount of evidence in favour of his theory, which reversed previous ideas and judgements by claiming that polychromed sculpture in all its various manifestations, and not sculpture of white marble, was the chief form in Antiquity: ‘On observe alors que la sculpture en pierre ne fut pas celle qui donna jadis le ton aux travaux et au goût des statues; qu’au contraire elle le reçut elle-même des autres parties de l’art de sculpter; de sorte que la matière de ses propres ouvrages ...
participa plus qu’on ne pense, du goût de variété, de richesse extérieure et de parure qu’expriment les mots de Sculpture Polychrome."  

Quatremer thought that the key to determining which techniques were used in Antiquity to polychromy marble sculpture was provided by a particular philological interpretation of the well-known passage in which Pliny the Elder reports that the sculptor Praxiteles valued especially highly those of his statues that had been coloured by the painter Nicias: 'Hic est Nicias, de quo diebat Praxiteles interrogatus quo maxime opera sua probarer in marmoribus: Quibus Nicias manum admovent; Tantum circumlimiti eius tribuebatur.'  

The painted decoration is here denoted by the term 'circumlimito', which Quatremer's predecessors, including the Comte de Caylus and the sculptor Etienne-Maurice Falconet, had interpreted as signifying varnish. Yet since Nicias painted in encaustic, Quatremer concluded that this must have been the technique employed to colour sculpture.  

Again, he supports his hypothesis by quoting other passages from Antiquity writings and by adding the empirical evidence of traces of paint on Antique sculptures that he himself had examined in Rome and Paris. Quatremer describes the encaustic technique as a way 'de colorer et de teinter les marbres, sans y produire aucune épuisement.' He adds: 'Ces teintes incorporées par l'encaustique, n'ayant aucune épuisement, et n'étant qu'une approximation du ton réel des objets, ne détruisaient pas l'opinion d'unité dans la matière, et pouvaient sembler n'être que le jeu des nuances d'un marbre que la nature se serait plus à diversifier.' Time and again Quatremer insists that Antique marble sculptures were not painted in the conventional sense but bore only 'teintes légères.' In his opinion the Parthenon and 'Theseion' sculptures were also tinted, in a way comparable to the hues displayed by camoes: 'sans être de la sculpture peinte, [ils] étaient ce que j'appelle de la sculpture polychrome, c'est-à-dire, qu'ils jouaient quelques-unes des apparences de la peinture, sans prétendre en faire les effets.' Quatremer supposed the latter type of painted sculpture to have existed only during the early period of Greek sculpture, which had thus attempted to satisfy the instinctual 'eye of a savage or child' by producing a complete illusion of reality.  

We now know that this monolithic view of the colouring of Antique sculpture, which permits works from the mature phases of Greek sculpture to be only lightly tinted rather than painted, is false. The fact that certain especially well preserved examples of polychromed Antique sculpture, such as the statue of Augustus from Prima Porta, were unknown at the time and that suitable methods of scientific investigation were not available no doubt explains this error.  

Even so, it is surprising that Quatremer — someone who otherwise always bore in mind the problems posed by the age of the sculptures and the loss of their polychromy — never seems to have considered the possibility that what presented itself in his time as a light tinting could originally have been a far stronger colouring. Moreover, it is striking that not once does he describe in detail colour traces that he himself saw, preferring instead to report on their general effect. One suspects that Quatremer's view of the polychromy of Antique sculpture was ultimately guided by notions he entertained as a Classical theorist of art, that the primacy of line and form and the strict separation of painting and sculpture simply did not allow him to conceive of Antique sculpture as 'painted'. He attacked his predecessors as subject to preconceptions because they had largely ignored the colouring of sculpture in Antiquity, but one could equally well accuse Quatremer himself of prejudice:

dice: he would seem to be interpreting evidence, even if less completely so than his predecessors, in subjective terms that, governed by specific notions of taste, represent an attempt to bring the results of empirical study into line with a particular theory of art. Hence, the term 'polychromy', coined by Quatremer in 1806 as an alternative to 'painting', originally possessed Classical connotations of which we are no longer conscious. The culmination of Le Jupiter olympien, prepared for throughout the book, is the attempted reconstruction of famous examples of the goldsmith's art from Antiquity, such as the legendary shield of Achilles, described by Homer and believed by Quatremer to have actually existed, and the cult images of gold and ivory from the time of Phidias, all known only from the writings of Antique authors. Quatremer's intention was not purely archaeological: his reconstruction of these works, which he terms 'incomparably the greatest masterpieces of Greek art', was to provide contemporary artists with a hitherto lost source of inspiration and models. He therefore illustrated his text lavishly with hand-coloured lithographs of the pieces he had reconstructed, turning the volume into a precious artefact.
of place went to the ‘Olympic Jupiter’, the colossal statue of the enthroned god that had been created for the Zeus sanctuary at Olympia and that lent its name to Quatremère’s study (colour plate VIII, fig. 3). Its reconstruction was based on the brief description by Pausanias and on coins, gems and other, comparable statues (fig. 4). Without his admitting as much, the poly-chromy – gold reliefs on variously coloured backgrounds and so forth – were largely the product of Quatremère’s imagination. Revealingly, the author encourages readers to understand his reconstruction of the statue’s colouring by thinking of Raphael’s decoration of the Vatican loggias. Quatremère employed the same method in reconstructing the other famous cult figures, whether it be the Parthenon Athena or Polyclitus’ renowned statue of Hera at Argos (colour plate VIII, fig. 2), both of them described by Pausanias and Tertullian. Such masterpieces of Ancient Greek art form the keystone of Quatremère’s book and he uses them to establish that Antique sculpture had always been coloured: ‘l’exécution de ces sortes d’ouvrages ont existé, et se sont soutenus dans tout les siècles, et à toutes les périodes des arts de l’antiquité’. With the notion that in Antiquity coloured sculpture was the rule, not the exception, Quatremère revolutionized the conventional view of Antique sculpture.

Convinced that the idea of beauty itself was reflected in Ancient Greek sculpture and needed only to be imitated by modern artists, Quatremère saw his comprehensive survey of colour in Antique sculpture as a contribution to contemporary art. However tenuous the link between the two, he continued to view archaeology as the servant of modern art or, as he put it: ‘nous appelons l’érudition au secours de l’art’. He was naturally aware that, as already noted, coloured sculpture contradicted Classical ideals of art. At the end of Le Jupiter olympien he therefore marshalled a wealth of arguments to reconcile archaeological findings with modern artistic doctrines, but his tortuous thought processes and often purely rhetorical language served only to make more apparent that the two were in fact irreconcilable. While accepting the principles of Classical theories of art, Quatremère time and again pleaded for exceptions to be made and for the theories not to be applied all too rigorously. His arguments encompass aesthetic effects, as when he claims that an affinity exists between the colour of gold and of ivory that annuls the chromatic monotony of a sculpture – what he calls, polemically, ‘the law of monotony’. He agrees in principle with the opposing view, that external lavishness obscures the idea embodied in a work of art, but feels that the importance of such abstract notions should not be exaggerated. In any case, an iconology of materials exists that can enhance certain of the work’s ideas. The beauty of colour is only an addition, but it does not detract from the beauty of the sculpture. Further, to the argument that sculpture is governed by form and not by colour, which in three-dimensional work can only blur the distinction between painting and sculpture and lead to excessive illusionism, Quatremère replies that, although this opinion is basically correct, the Ancients used colour not in the manner of illusionistic painting but simply to tint their sculptures. Here he confirms indirectly the suspicion expressed above that he interpreted empirical findings so as to bring them into har-

Fig. 5. Jean-Baptiste Clésinger, Woman Bitten by a Snake, 1847; coloured marble, Musée d’Orsay, Paris.

图 5. 克莱桑热：被蛇咬的女子，上色大理石，巴黎奥赛博物馆。
mony with an existing theory of art. Having set out to legitimize the use of coloured Antique sculpture as a model, Quatremère ends up by cutting the argumentational ground from under his own feet: in the concluding section of his book he points out that the ultimate purpose of colouring sculptures had been to provide convincing evidence of the existence of the gods, that art was practised in the service of religion, that it was therefore a part of history and, as such, could be understood only by applying historical criteria. It seems not to have occurred to him that, in thus allowing relativism to have the last word, he destroyed the very connection with modern art that he had wished to strengthen.

I think it will have become clear that archaeology and the theory of art are here incompatible. In fact, Quatremère’s book provides an exemplary demonstration of the epoch-making rupture between empirical study and metaphysical theory that characterizes the post-French Revolution world. Not only could the results of empirical research not be reconciled with the tenets of an idealistic theory of art; they actually called that theory into question, since they had shown that the Classical model differed from conventional views of it. The contradictions become even more glaring if one takes into account Quatremère’s theoretical writings. In Essai sur la nature, le but et les moyens de l’imitation dans les Beaux-Arts of 1823, for example, the Neoplatonic theorist of art even went so far as to promote the total lack of colour in sculpture, for, in encouraging imitation that consists solely in producing a similarity to the imitated objects, it aspires to a complete illusion, and that goes against the idea of beauty. The rift between Quatremère the archaeologist and Quatremère the theorist has here become quite obvious. Indeed, the findings of archaeology actually undermined his Neoclassical theories of art, developed as a vehement riposte to the Romantics and their notion of the Picturesque.

Quatremère’s inconsistency, ultimately the result of the increased historical and empirical awareness that marked the pursuit of knowledge in the second half of the eighteenth century, caused his theories about polychrome sculpture in Antiquity to meet with a mixed response. Stauneh supporters existed alongside opponents, among them the German art historian Friedrich Theodor Kugler who, himself a Classicist, claimed that the Ancients painted their sculpture in an even more restrained manner, not including the flesh in their colour schemes.

The limitations and contradictions inherent in Quatremère’s approach also become apparent in the discussions of colour in Antique architecture that were sparked off by reports of discoveries made in Sicily. Gripped by enthusiasm for Le Jupiter olympien, Jacques-Ignace Hittorff, a pupil of Charles Percier and a colleague of François Belanger, used finds made during excavations at Selinunte and Agrigento to propose that not only sculpture had been completely painted in Antiquity but architecture too, giving visual form to his ideas in an 1851 colour lithograph depicting the Temple of Hippodamus at Selinunte (colour plate VIII, fig. 4). This was far too radical for Quatremère. However, instead of taking part himself in the heated debate that ensued throughout Europe, he enlisted the services of Raoul-Rochette in attacking Hittorff. This was a matter of considerable delicacy because Raoul-Rochette, a younger colleague who hoped to become Quatremère’s successor as Permanent Secretary of the Académie des Beaux-Arts, had already published an article expressing complete agreement with Hittorff’s theories. Despite Raoul-Rochette’s intervention, the ghosts that Quatremère had aroused continued to haunt him: the idea that Antique architecture had been entirely coloured gained rapid and widespread acceptance.

Le Jupiter olympien also had an effect on contemporary art, although in 1815 widespread polychromy of sculptures lay many years in the future. A major early exponent of coloured sculpture was Jean-Baptiste Clésinger who, in Woman Bitten by a Snake (Femme piquée par un serpent) of 1847, used the encaustic method of painting marble described by Quatremère (fig. 5). Artists such as Edgar Degas (fig. 6), Gustav Klimt and Max Klinger were to follow suit in the second half of the nineteenth century. Quatremère’s work had caused a general increase in awareness of colour in three-dimensional contexts, leading eventually to research into, and reappraisal of, coloured sculpture in epochs other than Classical Antiquity. As late as 1866, for example, Eugène-Emmanuel Viollet-le-Duc, the great promoter of the Gothic Revival, explained his interest in the polychromy of medieval sculpture by referring to the fact that the Ancient Greeks had coloured their sculpture.

By proving that Antique sculpture had been coloured, Quatremère’s Le Jupiter olympien revolutionized modern images of Antiquity. I do not think it is claiming too much to say that, ultimately, we owe it to Quatremère that we are discussing with our Chinese colleagues methods of conserving Emperor Quin’s

Fig. 6. Edgar Degas. Little Dancer of Fourteen Years, 1878-81; bronze, cotton, satin and wood; Musée d’Orsay, Paris.

图 6. 德加：十四岁的舞女，青铜、棉、丝和木，巴黎奥赛博物馆。

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army of clay warriors and the history of Antique polychromy. Yet the work of this archaeologist and theorist of art, full of contradictions as it is, should also make us aware of how much we are tied to the times in which we live, of how relative each of our ideas and activities must be. Although all research and restoration work should aim to be free of preconceptions, Quatremer de Quincy reminds us this goal can never be attained completely.

(translated by Michael Foster)

Notes
1 'the great monsieur Quatremer de Quincy put in an appearance. He is the most tedious of all members of the Institute.' STENOINAL, 'Esquisses de la soeeit6 parisiene, de la politique et de la litterature: Esquisse XV (1827)', in idem, Paris-Londres: Chronique, ed. Renee Denier, Paris, 1997, p. 807. See ibid., p. 767, for a scathingly ironic description of a lecture given by Quatremer during a meeting of the Académie des Beaux-Arts in 1826.
2 For Quatremer's life, see esp. REINE SCHNEIDER, Quatremer de Quincy et son intervention dans les arts (1788-1830), Paris, 1910, and the brief account in SYLVIA LAVIN, Quatremer de Quincy and the Invention of a Modern Language of Architecture, Cambridge and London, 1992, pp. 2-4.
4 ANTOINE CHRYSTOSEMITE QUATREME DE QUINCY, Le Jeujipolympien, ou L'Art de la sculpture antique considéré sous un nouveau point de vue; Paris, 1815, dedication.
7 See JOHANN JOACHIM WINCKELMANN, Geschichte der Kunst des Alteimrs (1764), Darmstadt, 1993, p. 9: 'meine Absicht ist, einen Ver-such eines Lehrgebäudes zu liefern.'
9 'Winckelmann lent a great impulse to the study of Antiquity...by the single synthetic conception of his work.' QUATREMER DE QUINCY (note 4), p. VIII.
12 'Winckelmann could not encompass, perhaps not even sense, all the points surrounding his field of study.' QUATREMER DE QUINCY (note 4), p. VIII.
13 'The new historiographer of Antique art [i.e. Winckelmann] did not progress far in knowledge of the genres that make up sculpture...he cast only an uncertain eye and threw only a weak light on that which determines the various manners, the different techniques used to produce the works of art, the diversity of taste, of effect, of composition and of the genius of each genre.' Ibid.
14 See WINCKELMANN (note 7), pp. 30-2.
15 Since white is the colour that sends back the greatest number of light-rays, and in this respect, a beautiful body will be more beautiful the whiter it is.' Ibid., p. 148.
17 'I flatter myself...that I have extended this new domain of Antiquity and destroyed prejudices, some of which seem to me to have their source in a complete lack of observation and in ignorance even of facts.' QUATREMER DE QUINCY (note 4), p. XX.
18 'For...knowledge [of polychrome art] has hitherto been lacking in histories of Antiquity because artists have never been guided by the practice of modern sculpture to search for an art of assemblage or for works made of various materials.' Ibid., p. XIII.
19 In spite of the statement of his just quoted, Quatremer could have found support for his study of Antique polychromy in the sculpture of his own day, which was gradually beginning to introduce colour. One thinks, for instance, of Antoine-Denis Chaudet's personification of Peace, made from variously coloured metals in commemoration of the Treaty of Amiens and displayed in 1806 in the Salon de la Paix in the Tuileries Palace. For detailed discussion of this and other examples, see SCHNEIDER (note 2), pp. 126-8; DAVID VAN ZANSTEN, The Architectural Polychromy of the 1830's, New York and London, 1977, pp. 24-7; and ANDREAS BLÜHM, 'In Living Colour: A Short History of Colour in Sculpture in the 19th Century', in idem, ed., The Colour of Sculpture (1840-1910), exh. cat., Amsterdam, Van Gogh Museum, and Leeds, Henry Moore Institute (Zwolle, 1996), p. 16.
20 'the ancient world is starting to form a parallel to the modern world.' Quatremer de Quincy (note 4), p. II.
21 'the immense void that time and destruction have left between the Ancients and us.' Ibid., p. III.
22 'One must persuade oneself that the Ancients used the arts quite differently from the Moderns.' Ibid., p. 32.
23 'One must...in order to judge well, come close to the type of taste peculiar to these works, to the causes that produced them and to the effects demanded of them. One ought not to isolate the monuments from the opinions, feelings and affections that gave birth to them.' P. XXV.
24 'One must judge things solely on their own terms.' Ibid.
26 See ibid., pp. 8-10.
28 See QUATREMÈRE DE QUINCY (note 4), esp. pp. 34-6, 40-2 and 54-5.
29 'Imagining these great works of art, the fame they enjoyed, the celebrity of their creators, I became more and more astonished, also by the silence of modern critics about such a noble area of Antique art.' Ibid., p. X.
33 'Without being what one might well call painted... [the sculpture] had parts tinted in various ways, sometimes placing it in contrast to the background to which the colours were applied, sometimes indicating the plane in which the figures were situated by various hues, whether on the drapery or on any of the many other details.' QUATREMÈRE DE QUINCY (note 4), p. 31.
34 See ibid., p. 31.
35 See JOHANN D. AKERBLAD, Sobre duas luminite de bronze, trouvée ne ' consecrations d'Atene: Desseret d'un membro ordinario dell'Academia libera d'Archeologia di Roma, Rome, 1811, pp. 9-10, and EDUARDO DODWELL, Alcuni bassrelievi della Grecia, Rome, 1812, p. VI. Quatremère de Quincy (note 4), p. 32, cites only Akerblad's work.
36 See QUATREMÈRE DE QUINCY (note 4), pp. 33-5.
38 'One sees, therefore, that it was not stone sculpture that once set the tone for the works and the taste of sculptors, but that, on the contrary, sculptors in stone took from other areas of the arts of sculpture, so that the materials of their own work... played a part, larger than hitherto supposed, in a taste that was governed by variety, by external richness and by decoration, and that is denoted by the words Polychrome Sculpture.' Ibid., p. 44.
39 'This is the Nikias of whom Praxiteles, asked which of his marble works he liked best, replied: those in which Nikias had a hand. That is how he valued his colouring.' PLINY THE YOUNGER, Historia Naturalis, XXXV, ed. Roderich König, Darmstadt 1997, p. 133.
40 See QUATREMÈRE DE QUINCY (note 4), pp. 45-6.
41 See ibid., pp. 49 and 52-4.
42 'Of colouring and tinting marble sculptures without producing any thickness.' Ibid., p. 49.
43 'The tints provided by encrustation had no thickness whatsoever, were no more than an approximation to the actual colour of the objects, did not destroy the impression of the material's unity and could appear simply as a play of nuances in a piece of marble that Nature had been pleased to diversify.' Ibid., p. 50.
44 For mention of these 'light tints', see ibid., pp. 29, 31, 33, 36, 53 et passim.
45 'without being painted sculpture, [they were] what I call polychrome sculpture, that is to say, they enjoyed some of the features of painting without pretending to imitate its effects.' Ibid., p. 32.
46 'To eal un sauvage ou d'un enfant.' Ibid., p. 3.
48 See QUATREMÈRE DE QUINCY (note 4), esp. p. 29.
50 See QUATREMÈRE DE QUINCY (note 4), pp. 64-387.
51 'sans aucune comparaison les chefs-d'oeuvre de l'art des Grecs'. Ibid., p. XVIII.
52 Ibid., pp. XVI-XVIII.
54 See QUATREMÈRE DE QUINCY (note 4), pp. 268-70.
55 See ibid., p. 279.
56 See ibid., pp. 219-21 and 326-8.
57 'works executed in this way existed, and they existed throughout all the centuries and periods of the art of Antiquity.' Ibid., p. XIX.
58 See also ibid., pp. XX-XXI.
59 See ibid., pp. IV, XXIII and 29.
60 'we appeal to learning to help art.' Ibid., p. IV.
61 See ibid., pp. 388-90.
62 'la loi de la monotonie'. Ibid., p. 390.
63 See ibid., pp. 390-1.
64 See ibid., p. 391.
65 See ibid., pp. XXIII-XXV and 392.
68 See REUTERSWÄRD (note 47), pp. 28-9.
69 See MIDDLETON (note 49), pp. 175-7.
73 See EUGÈNE VIGILÉE-DEUX, Dictionnaire raisonné de l'architecture française, vol. 8, Paris, 1866, p. 275: 'Le moyen àge a très-fréquemment coloré la statuaire et l'ornementation sculptée. C'est encore un point de rapport entre ces arts et ceux de l'antiquité grecque.'
奥林匹克的朱庇特像及古代雕塑彩绘的再发现：
在经验研究和审美理想之间徘徊的卡特勒梅尔·德坎西

克尼平

后来通过它的小说《红与黑》闻名的司汤达。在 1827 年给《新月刊》写的一篇文章中，对柏文和纯文学学院的一次会议做了报告。他以贬低的口吻评论考古学家和艺术史家卡特勒梅尔·德坎西：“......伟大的卡特勒梅尔先生露面了。此人系整个学院所有院士中最无聊者。”这轻蔑之词掩盖着一场浪漫派和古典派之间的斗争，有时颇为激烈的有关艺术理论之争，卡特勒梅尔在官方美术学院任职，他在这场争论中自然固守古典派的立场。而在考古学领域，卡特勒梅尔无疑属于——这里我们不禁要反对司汤达的意见——最有意思而又最具创新精神的人物。他的意义首先在于他是研究古代雕塑彩绘的先驱。

但是我们下面要关注的乃是他的著作《奥林匹克的朱庇特像，以新眼光看古代雕塑艺术》。此书于 1815 年出版，作者将它作为“非常谦恭和真诚的主题”献给了皇帝陛下拿破仑。在这含糊其辞的书名之后所隐藏的正是第一部古代雕塑彩绘史。按照当时的观点，此书的重点自然放在古希腊的雕塑上，探讨古代彩绘的艺术，几乎不引用此书，尽管如此，事实还是令人惊讶，因为迄今为止，还没人特别从方法论和社会学价值上对这本著作作出评价。

历史学家米歇尔·福柯在其那给人印象深刻的《词与物，人文科学考古》一书中，依据他对不同领域如生物学、语言学和经济学的研究，展示了 18 世纪中思想的变革，这一变革来自走向怀疑和认识以及用语言表现世界是否可能，但引发两个彼此相反的方向发展的思想运动：即作为 18 世纪经验主义之继承但更为激进的实证主义和作为复兴形而上学地解释世界之尝试的唯心主义。在此当中，卡特勒梅尔·德坎西采取的是奇特的模棱两可的立场，其原因在于他扮演考古学家和艺术理论家的双重角色时所产生的冲突。

卡特勒梅尔·德坎西完成他所彩绘雕塑史耗费了 30 多年的精力，他以试图对考古学进行革命并想为它增加一门新的、要整个改变这个学科的专科。他亲身参与研究和学科的现代研究者。这部彩绘从 18 世纪下半叶一直持续到 19 世纪中叶。在考古学领域，约翰·约阿希姆·温克尔曼实现了这一目标，他 1764 年出版的《古代艺术史》给读者留下深刻的印象。温克尔曼借此要对学科的整体体系进行尝试。卡特勒梅尔也了解温克尔曼作为现代考古学奠基人的革命意义。在他那奥林匹克的朱庇特像的专著前言中，他承认除了那些他在罗马和那不勒斯所见的古代艺术品之外，正是温克尔曼的著作唤醒了他对古代雕塑的激情。他在评价他对此考古学的意义时说：“通过他著述的独一无二的综合性构思......温克尔曼对研究古代的巨大推动作用。”卡特勒梅尔也在试图进行综合性构思，即要求一种总结各项观察结果并与彼此联系进行概述的描述方式。他若要作出与温克尔曼那样的建树，他就得对温克尔曼做相对的评论，在某种程度上他还要对古典考古学创始人克吕斯伯爵那样做解构处理。卡特勒梅尔在学术上取得的成功甚至还要间接地感谢他，他得奖著名的克吕斯奖。卡特勒梅尔尝试新考古学，目标及其明确，意识及其坚定，今日的读者对此会感到诧异，他有目标地引入——借用库欣的术语——范式的转换，他的著作为了了解他的这一步往往提供了一个范例。科学理论家托马斯·库恩指出，“正常科学”系由某种范式确定，它不停地确凿重要的事实、事实和理论的关系以及理论的描述，在“正常科学”中，不时会出现不确定和危机的时刻。不能解释的异常情况会给他这个专业带来不安，这种情况下便需要寻求新的解释模式。这些模式只有通过相应的宣传，然后建立起新的范式，才有可能在一个研究群体中得到贯彻。在卡特勒梅尔的时代，令人不安的异常情况是古代雕塑上的彩绘残迹以及由不同颜色材料制成的雕塑，它们无法与当时广泛流行的古代雕塑为单色的形象相吻合。说到这里，成功地宣传和贯彻新的范式，必然少不了一些专业带头人的“众神的黄昏”。与此相应，卡特勒梅尔在其 1815 年的著作中先是毫不犹豫地赞赏温克尔曼，接着对他的不足表示谅解：“温克尔曼在其研究的领域未能面面俱到，也许也未能意识到。”“他总是反复地使自己感到：......新的古代艺术史家尚未达到把握雕塑的认知的深度，......他的眼光并不敏锐，至于各种做法取决于什么，艺术品的非同寻常，趣味、效果、构图乃至不同门类的天才的异变，对这些问题，他均未能透彻。”卡特勒梅尔的批评并非溢美之词。温克尔曼尽管在他的《古代艺术史》中提到涂着红色的希腊陶俑，包括部分包含的雕饰；由黄金和象牙作的雕像和镂于木、头和手部由大理石组的雕像，他还提及着衣的雕像以及一座 1760 年在海格立斯城发现的狄安娜像，其头发和长袍均彩绘，然而这些艺术品不是被粗糙地归入希腊雕塑尚不发达的早期就是被简简单单地列举，仅单色雕塑仍是常规，这样彩绘意义便未得到正确的认识。对温克尔曼而言，就象他对他的同时代人那样，白色大理石雕刻不曾希腊化成艺术的常规和表意，就是以他所独具一格的较实质性古代研究而对温克尔曼有重大影响的克吕斯伯爵也偶尔在《绘画和纯文学学院的论文集》或是在他那于 1752-1767 年间发表的代表作《古代埃及、伊特拉河、希腊和罗马艺术集》中提到彩绘痕迹或是不同颜色材料的雕刻，他认为这些现象并不重要并把它们作为偏离正道的古代趣味加以拒绝，态度上比温克尔曼还要坚定。对古代彩色雕塑无动于衷和拒绝的态度，根据结局还是受到当时占领统治地位的古典艺术理论的影响，古典艺术理论对雕塑和绘画作严格的门类等级区分，雕塑以其形式界定，如素描或线条，形式本身便能反映出天才
般的创造活动尤其是艺术品的思想。卡特勒尔对此深有感应。他以启蒙的姿态登台，意在摧毁研究中的偏见思想。他自信地写到：“我可以自信地，我要扩展古代研究的这一新领域，消灭偏见，看来有些偏见的根源在于完全缺乏观察和对事实无知。”作为保有的分析家，卡特勒尔认为造成这种无知除了有学术艺术理论的影响外，也与现代艺术家的实践有关。尤其是对于现代雕塑创作的艺术影响不言而喻，因为现代雕塑常被看作是大地艺术、景观艺术和大地艺术的相矛盾，而且由于现代雕塑创造出人对大地艺术的雕塑作品，从而确认了审美习惯，深受艺术理论和艺术实践影响的考古学家因此便不可能看到现代雕塑的根源。对于当时的世代来说，卡特勒尔阐述的这些正是令人惊讶的、相对主观的认识，即思想乃是受到当时制度的观念决定的。

正是由于有了这种对历史修约的敏锐意识，卡特勒尔才能可能冲出这种循环论证。可以不过分地说，幸亏有了现代早期的历史意识，古代雕塑彩绘的现象才得到了认识以及相应的评价。历史意识的一个十分重要的组成部分就是对人之间和时代之间的关系意识。这一点在卡特勒尔身上表现得再清楚不过了，他这样说， “古代世界正与现代世界的对照”，他强调 “从古至今所流传的时光和带来的破坏留下了无法估量的空白。” 卡特勒尔有常态常被引用的话语，但被误解为观念的经验之谈，它再不过时地表达了对差别的这种历史意识： “要相信，古人与艺术的利用与现代人完全不同。” 按卡特勒尔的观点，古代艺术不同于今日，是因为它在不同的社会环境下生成的，因此艺术只有通过其时代的产生和历史条件才能了解和评价；“为了判断正误，就得从作品产生之因及其当时所具有的作用中来理解这些作品特有的趣味种类。” 这些想法最后汇集到看来在利奥波德 - 兰克之间的一句话：“判断事物必须从事物本身出发。” 在法国，这种符合古代明显带有历史性的保留眼光的历史思想根源在于 “古代与现代之争”。 卡特勒尔是法国 1878 年大革命的积极参与者，倘若他本人没有经历其间由政治社会条件所决定的世界迅速变化和可变性，他对历史不会采取这一种一成不变的态度。

让我们回到彩绘问题上来：促使卡特勒尔对古代雕塑创作的历史现象进行革命的还有那些无法解释的异常情况，古代作家保萨尼阿斯和普利克尼在他们的著作中便提到了古代雕塑的色彩，介绍雅典发现的神庙有这方面的描绘。卡特勒尔自己在海格立斯城和庞培发掘现场，在意大利尤其是罗马的众多博物馆以及拿破仑博物馆，今日已被罗马卢浮宫，也观察到这些异常情况。特别是保萨尼阿斯对今已不存的由菲迪亚斯所用黄金和象牙制成的神像的描绘，吸引着人们研究多种颜色和材料的现象的兴趣和单色，对已失像的描绘还包括第一批对雅典帕台农神庙和忒修斯神庙雕像颜色残迹的描绘。卡特勒尔从未到过希腊，但他与 19 世纪初参与拆卸帕台农神庙所用埃金金矿工作的锡瓦塔洛 - 卡西弗、工程师和热洛以及律师的法国大使福尔克联系，他们多次向他证实某些颜色残迹的存在。 帕台农神庙的雕刻装饰原来彩绘的着色通过斯图尔特和里德研究的结果得到了证实，1878 年出版的《雅典古迹》一书记载了他们的观察结果，其中包括许多用于加固金属连接和标志的钻孔。卡特勒尔由此作出推论，颜色痕迹是原有的。卡特勒尔从他的情报人士对帕台农神庙的雕刻色彩的观察得出结论： “这些雕刻不能称之为画过，它们有的地方以不同方式上了色。 如同使雕刻突出于涂了颜料的背景，其时又通过不同的色调，或是通过许多其它的局部来显示雕塑的层面。” 即使在巴黎，卡特勒尔也使自己坚信色彩的存在，这是因为拿破仑博物馆藏有一张古代神庙雕塑的残片，按习惯作风，人们对残骤做了除污处理，将当时其意义尚未被认识的局部颜料痕迹一并清除。不过卡特勒尔认为，当残骤还在运输箱中时，他曾见到色彩痕迹，只是记得那么清楚罢了。 1811 至 1812 年间，考古学家阿克雷尔和莫德维尔的著作问世，书中亦指出，雅典忒修斯神庙有色彩遗迹。

除了提及雅典著名神庙的雕刻装饰的色彩之外，卡特勒尔将他当时所知具有彩绘痕迹的所有雕刻作品都汇编，引用了古代文献，材料翔实。在使用多块石料制作雕刻的领域，在彩绘处理的青铜雕像领域，他也作了同样的尝试，尤其是海格立斯城和庞培的发现让他高兴，这样他便为他的理论提供了确实的证据，即将其汉族的和观点和价值标准一举颠倒了过来。在古代雕刻中，各种神庙的神像有色彩，而各种色彩的多米尼雕刻。确定大理石雕刻着色技术的关键，卡特勒尔认为有著名的普林尼在著名的普林尼文集中有更为详细的描述，普林尼讲，雕塑家米拉克西斯特对他的那几座由画家尼基亚斯彩绘过的雕刻有钟情。那儿使用了概念 “circuminculo” 来形容彩绘，卡特勒尔的前辈如凯伊或者雕塑家法尔内科把它解释为清淡。由于尼基亚斯是这一类用蜡描绘的画家，卡特勒尔推断，雕刻的彩绘必然使用的是这一技术。这一设想也在其他古代著作中所引用，同时通过对收藏在罗马和巴黎的古代雕刻上的颜色遗迹的验证得到了证实。卡特勒尔将用蜡描绘彩绘雕刻的效果描绘成一种 “给大理石染色和上色而又不造成表面堆积” 的技术，他在他的著作中一再固执地认为，古代大理石雕刻不是给有重彩，而是未用颜料。他将帕台农神庙和忒修斯神庙雕刻装饰与浮雕宝石作色结构上的比较，象牙已流落的理论，他发现那些雕刻装饰上涂了 “不但是浓彩的雕刻，我称它们为彩绘雕刻，也就是说，它们有些绘画的特征，却不易模仿绘画的效果 ”。这种色彩上涂的雕刻，在卡特勒尔看来，当属古希腊雕刻的早期，那时的人们本能地以 “一个野蛮人或一个孩子的眼睛” 试着借此造成一种彻底彻底的幻觉。正是我们今天所知，就古代雕刻彩绘而论，这种只许古代盛期有淡抹而不容有浓彩的观点乃是错误的，造成错误的认识原因在于，一些保存状态不佳的古代彩绘雕刻如普雷米加斯特和所古斯都像还未被发现，再就是广泛缺乏合适的技术检验手段。同时这也是怪事，卡特勒尔明白清楚雕刻的年代和古老的位置，但他却不考虑，此时的浅在着当时有些表现更为强烈的色彩。还有一点十分重要，他在谈论颜色残迹时，从未作过近现代技术上的描述。所表示的不过是对他色彩问题的印象而已。这也使他发现作品，把古代雕刻的彩绘形象与浮雕的色彩的终究不同别人，而是艺术史家和古典主义者卡特勒尔，他重条纹和条式，区分雕塑和绘画的以各等级，自然不能允许 “彩绘的” 古代雕刻。因此人们也可以把他在反对他的无视线的前辈所说的话来指责他： 偏见！我们将会看到，虽然比他的首
辈更有限。为了使艺术理论和经验相一致，他也赋予经验科学一种与趣味判断相关的、受时代制约的主观性解释。卡特勒梅尔 1806 年第一个使用多色概念，它初期作为“彩绘”相对的概念而具有古典主义的色彩理论，今天使用它时，我们已经被意识不到层含义了。

其书的高潮，乃是卡特勒梅尔尽各种努力对古代著名的金银制品的复原所作的尝试。这些作品包括传奇性的由荷马描述过、但卡特勒梅尔却信以为真的阿喀琉斯的盾牌，尤其是菲迪亚斯时代完成的由黄金和象牙制成的神像、这些神像已无一存世，仅见于古代作家的记载。位于中央的乃是提到的奥林匹亚的朱庇特神像，这座端坐的巨像是菲迪亚斯为奥林匹亚宙斯神庙制作的。该像的复原是借助于保萨尼阿斯的简短描述以及参考硬币、浮雕宝石和可作比较的雕像完成的，复原的颜色，多为各色衬托的金属浮雕等等。在很大程度上出乎想象，虽然作者并没有承认这一点。

卡特勒梅尔坚信，在希腊雕刻作品中，美的观念会自行再现，现代人只需模仿即可。他想用古代雕刻的彩色史为当时的艺术发展作贡献。尽管谈不上成，他还是坚持他的考古学是现代艺术的仆人的观点不放，如他说到：“……我们呼唤学识为艺术服务。”这当中他当然意识到，这已让人感觉得出——在原则上，雕刻的色彩与古典的艺术教条是矛盾的。因此他在他的著作的结尾处找了不少和解考古学和现代艺术教条理由，这些编织一团，常常停留在修辞上的论证反而更加清楚地表现出两者的不可调和的。在论证方式上引人注目的是，卡特勒梅尔接受古代艺术理论的原则，但他又再无为规则的例外辩护，而且贬低理论上的严肃主张。可是他也在美学上初涉色彩的作用，如在黄金和象牙中间色色调的“友谊”，它可以在雕刻色彩的单调作用。这种方法被他论战式地称作“单色原则”。反对雕刻外表的华丽及奢侈的理由，因为这与艺术品的价值格格不入，他认为在原则上是正确的，但是抽象的原则不应过分夸张。决定雕刻的是形式而不是仅透过门类界限而造成决定错觉的色彩，他承认，从根本上来说，纵使这种论点也是正确的，只不过古人给雕刻上色并非要追求错觉绘画的效果，他。

我想，考古学和艺术理论在这里不再合体，这一点已显而易见，为了对现代早期而言，经验研究和形而上学理论之间的分离乃是意味深长和具时代意义的，卡特勒梅尔的著作恰恰为我们了解这个时期艺术理论的矛盾提供了一个范例。经验研究的结果和艺术理论的设想不再协调一致，它甚至还向后接提出了质疑，很清楚，古典艺术理论以前的榜样与人们那时想象的有出入。

这种在 18 世纪下半叶由对科学进行历史化和经验化造成的内在矛盾，也是造成接受卡特勒梅尔关于古代彩色雕刻理论时意见相左的原因，除了热情的拥护者之外，也有像埃米利奥·库尔多·塞勒这样的反对者，库尔多虽然同样是古典主义者，但他更为严厉，他只赞成非常有限的、大理石局部的彩绘，连肉色部分都不提。卡特勒梅尔 1815 年发表的著作也在同时代的雕塑界掀起了波澜，只是还要等几十年，彩色雕塑的艺术问题才得到了广泛的探讨。1847 年创作《驱蛇咬的女子》(巴黎奥赛博物馆)的让-巴蒂斯特·克莱桑热属于色彩雕刻的前驱，他在给大理石上色时使用的就是卡特勒梅尔描述过的蜡画法，在他的继承者有 19 世纪下半叶的艺术家如德加、克里姆特和克林格尔，卡特勒梅尔·德坎西以其论奥林匹亚的朱庇特像的著作，提出了古代雕刻是有色彩的证据，作为为现代的古代形象的革命作出了贡献。当前，我们同大多数人会一起探讨保护兵马俑的方法和古代彩绘，这还会特别感谢卡特勒梅尔，说这话当然未言过其实。同时，作为考古学史和艺术史的这么一个充满矛盾的人物，也应提醒我们，我们的努力要合乎时代潮流和它的相对性，毫无成为应该成为所有研究和修修补补工作的目标，即使完全实现这个目标最终只是幻想也罢。

(德译：陈锦林)
Antique Greek sculpture was at all times polychrome. The sculptures were made of different materials, but their polychromy always lead to a homogenous aesthetical effect. An antique Greek clay figure would first of all be covered with a priming of white stucco, limestone fragments with marble stucco, in order to create the illusion of a marble sculpture. Whereas abundant polychrome fragments and even intact paint layers are preserved not only on Greek terracottas (Colour plate front cover) but also on early Greek limestone sculpture, there are few preserved traces on the works of art in marble.

In the last years the polychrome paint layer of Greek marble sculptures has been extensively examined in a research project, largely financed by the „Deutsche Forschungsgemeinschaft“ using foremost scientific examination methods. With the help of technical photography, especially different shooting techniques in ultra-violet light, but also a special side-light technique many traces of earlier painting could be observed and documented. Chemical analysis of the pigments and binding agents as well as intensive microscopical analysis accompanied the documentation. For some of the figures it was possible to recover the almost complete form and polychromy of the paint layer. These findings led us to consider reconstructions of the sculptures using moulded stone copies.

The figure of the Archer on the West-pediment of the Aphaia Temple at Aegina, the kneeling Archer, dating from the early 5th century BC and created in Greece wears an oriental costume: a type of pullover, close-fitting leggings and a jacket (colour plate IX, fig. 4).

The surface of the figures on both pediments of the Aphaia Temple show only sparse traces of red, green and blue colouring. The use of gold-leaf on the pediment warriors has also been established. At the time of the excavation of the Archer in 1811, the discoverer Charles Cockerell and the architect Jakob Ignaz Hittorff, who was very interested in questions concerning polychromy, believed to have discovered the coloured shadow (ghost) of a costume of scales. More information has not been passed down by the excavators, whose account on the polychromy was otherwise very keen and correct. Adolf Furtwängler, who did further excavation work and research at the site of the sanctuary in 1901, devoted a lot of attention to questions concerning the polychromy of the pediment sculptures. He ventured a complete reconstruction of both pediments from the west and east side of the building (colour plate IX, fig. 2). However, only the colours blue and red were used, because these were the only pigments which had at that time been discovered on the originals.

Due to the lack of any traces of colour on the Archer, he reconstructed this figure in close accordance to the so-called Persian Horseman (colour plate IX, fig. 5), a fragmented marble sculpture, which had been found on the Acropolis in Athens shortly before the turn of the century. This sculpture has an unusually well preserved paint layer (colour plate IX, fig. 1). The horseman wears the same type of close-fitting leggings and jacket. A lozenge-shaped ornament is painted on the leggings; the jacket it decorated with slightly displaced lanes of scales.

The polychrome paint layer of the Persian Horseman is quite elaborate, but the coloured ornamentation of the Archer on the West-pediment of the Aphaia Temple exceeds all expectations. Photographs, shot in ultra-violet light and with raking light, made with the help of a number of colleagues since the 1980's, clearly show the splendor of the original sculpture.

On the ultra-violet-reflex shot of the leggings (colour plate IX, fig. 3), one can see a type of weathering, which most probably resulted from the different fastness of the pigments used. The complicated ornamentation, which originally decorated the complete leggings can be seen on this weather-worn area on the photograph: interlaced lozenge-stripes with lancet-shaped tips, which are again filled with small lozenges.

Using side-light, one can see a far more intense weathering on the sleeves, due to mechanical abrasion. This proves that leggings and upper garment were differentiated by their ornamentation. The sleeves of the „pullover“ were covered with lozenges, with every second lozenge-strip again filled with small lozenges.

The findings on the jacket of the Archer are spectacular. The hem was trimmed with a sumptuous ribbon. Painted animal pairs, face to face in combat position covered the main areas of the jacket. Again using side-light, the rear region of a griffon can clearly be seen. The preparatory work that the artist did on the marble surface is of exquisite precision: using a metal graver each feather quill was individually grooved to form a tensioned swoop. Remarkable is that the lowest, that is the smallest feather quill is just 1 to 2 mm wide. This type of love to detail surprises, on account of the fact, that the figure is positioned at least 12 meters above the viewer.

Due to the different weathering of the individual coloured areas, which can be seen using raking-light as well as in ultra violet light, it is possible with high certainty to determine certain pigments. This procedure can be confirmed in the comparison with late archaic Greek sculptures, which show definite traces of polychromy. One of the best preserved examples to compare is the above mentioned Persian Horseman from the Acropolis in Athens. Here one can observe creative features in general, typical for Greek sculpture around 500 BC: colours are always applied with the greatest possible contrast. This enhances the recognisability of the elaborate ornamentation. The choice of pigments is also canonical: for blue and green the copper-carbonate azurite and malachite are used, for red a natural cinnabar or red ochre. The brown and yellow tones were produced by using ochre.

Our reconstruction, which was realised on a marble mould copy considers all observations and possibilities concerning the analogy (colour plate IX, fig. 6). Natural pigments, similar to those found in Antiquity were used. For the outer side of the Archer's bow gold-leaf was applied. The naked skin was painted with haematite, a pigment, which was last discovered on the colossal kouroi of Samos.
古希腊雕塑彩绘 — 以埃吉那岛阿菲亚神庙神殿前三角板上的弓箭手为例

各个时期古希腊雕塑的材料各异，但这些雕塑都有彩绘，每幅上色，总能达成统一的审美效果。为了获得象大理石雕刻的表面肌理，一件古希腊的陶雕像用白石灰，而石灰岩雕像甚至会使用仿大理石的石膏打底，这使得使我们还能在希腊的陶俑身上（彩图，见封二）1，包括希腊早期的石灰岩雕刻的表面，发现残留下来的丰富颜色。有时甚至能在看见完整的彩绘层，但大理石雕刻上的彩绘痕迹却也不常见。

近几年，古希腊大理石雕刻的彩绘得到了系统阐明，这个科研项目主要是由德国科学基金会赞助的，在项目中，自然科学的研究方法占有突出的地位，借助于考古摄影的手法，尤其是在野外雕刻的摄影技术和专门的设备，可以观察和记录许多当时未被发现的记录的相机时，对彩绘和粘合剂的进行了化学分析，并作了大量的呈显分析。最后，在几座雕像上，几乎完整地重新获得了其彩绘的形和色。这些结果引起了我们思考，通过人造石模型来研究彩绘。

埃吉那岛阿菲亚神庙神殿前三角板上的一个弓箭手像

这个塑像手像创作于公元前五世纪初的希腊，它看起来是人一件毛衣，一条长身裙和一件夹克（彩图 IV, 4）。阿菲亚神殿前三角板上的雕像表面只留下不多而且很明显的红、绿和蓝色痕迹。在三角板上的战士身上使用了金箔，在此期间也发现了迹象。当弓箭手像于 1811 年发掘时，发现者查尔斯·科克雷尔和对彩绘问题极其关心的建筑家雅各布·伊格内茨·希托夫都以为看到的是狮身的影子（ghost）。发掘者没有给我们提供更多的信息，尽管他们对彩绘作了十分充分和忠实的说明。

阿道夫·富特文勃于1901年对神庙做了新的发掘和研究，对三角板上的雕刻彩绘问题，他重新予以关注，他大胆地复原了神庙西、东东西的两块整三角板（彩图 IX, 2）。但他把颜色局限于蓝和红色，因为当时在原作上还设有观察到其他的颜色。

由于弓箭手中缺乏彩绘痕迹，在复原时，富特文勃依据的是所谓的波斯骑士（彩图 IX, 5）。这是一件残破的大理石雕像，它是在以前没有几年在雅典卫城发现的，其彩绘保存状况未佳（彩图 IX, 1）3。这个骑士亦着套身裤和夹克，裤子上画着菱形纹饰，夹克上装饰有稍微偏移的鳞片。

波斯骑士的彩绘已经十分讲究，但阿菲亚神庙前三角板上的弓箭手的彩绘装饰却超出了所有人的期望。紫外线照相和用 80 年代以来一些同事研制的滤光片所拍的照片，再现了这座雕像的华彩。

在雕像的紫外线反光照片上（彩图 IX，3），可以观察到一种反光，这是由于不同颜料的牢固性各异所至。在这张反光照片上可以看见有光泽点的图案；交错的菱形带，柳叶刀般的菱点，里面又布满小菱形。在雕像的袖子上，这一次通过侧光，可以看出极深的，受力造成风化，这表明，袖子和衣领装饰的不同而明显有别。“毛衣”袖子有菱形纹饰，隔一排的每个菱形中又布满小菱形。

最轰动的最后还是在弓箭手的夹克上的发现，衣袖由绚丽的带子作装饰。夹克的下端面上画着成对的动物，它们对视，据摆动的架式，使画面活跃。最外，一只巨鸟的下半身清晰可辨。画家在大理石表面上的羽绒，充满张力，艺术家用金属雕刻刀把它们一丝不苟地刻出来。值得注意的是，最下面的，也是最小的羽绒仅有 1 至 2 毫米宽。这件探在观者头上至少 12 米高的雕像竟如此讲究细微，令人吃惊。基于不同的表面风化程度的不同，这在侧光下和紫外线下均能区别，便可相当有把握地将某些颜料鉴别出来，通过与彩绘痕迹较为明显的古风晚期的希腊雕塑进行比较，这种方法显得更有说服力。保存最好的、可以比较的例子之一，便是上面提到的雅典卫城的波斯骑士像。这是可以看到适用于公元前 500 年左右希腊雕塑的一般造型方式。设色时，相邻的颜色的反差总是愈大愈佳。这使人们对将辨别精巧的纹饰。而且颜料的选择也是有规范的：蓝色和绿色多为碳酸铜石膏和孔雀石，红色是天然朱砂或红赭石，褐色和蓝色则是用朱砂石与铁粉制成的。

在用彩在将模型进行复原时，我们考虑了具体的，所有情况和可能性（彩图 IX, 6）。因此，我们用的是与古希腊颜料相同的天然颜料。4 弓箭者的外衣的金色使用的是金箔。金属的皮肤系用赤铁矿作颜料画的。在此之前，萨摩斯岛的庞大少年雕像上也证实了这种颜料。

注：
1. 参见英文文注 1。
2. 参见英文文注 2。
3. 参见英文文注 3。
4. 这里要特别感谢多丽丝·劳恩施泰因·森女士。
5. 红色=朱砂/蓝色=石青/绿色=孔雀石/金赭石和赭墨色。
6. 参见英文文注 6。
战国时代纺织工艺中的染

中国服饰的颜色扮演很重要的角色。它不仅要区别场合，还要显示地位。荀子(约公元前313-230)在书中提到“天子袍衣是衣，诸侯常袍衣，大夫袍衣，士衣简衣”。不只服装颜色有别，其他服饰、用品也有颜色上的差异，如“诸侯衣衫，大夫营守”。这种区别贵族、长幼和贫富的规定。古代称之为礼。

《周礼》及《仪礼》等经书中详述周代(公元前1027-前221)的服装制度，但是这些经书的内容已加汉代(公元前206-公元后220)儒者增补，可靠性受疑。有些书，如《墨子》、《韩非子》、《管子》等也有后人或其弟子增补。因此，那些礼制的开端很难确定。尤其服饰中色彩配合五行、五方和季节观念在战国(公元前475-前221)晚期才逐渐形成，吕布韦书于战国长篇中未见。今于《日书》中完善形成相克的观念，试图说明秦国取代周朝是合理的。而《周礼》中又记载类似内容，导致先秦难以厘清的困难。因此，本文将战国时期服装的发展报告为主，整理出当时常用的颜色，配合历代以前的文字资料，探讨当时的文字和衣饰方法。

从子书中许多与色彩有关的语句，如“不白不白，涅而不得”，“白者未在涅，而与之俱白”。“青取之于蓝，而青于蓝”。“染之甚者，染于黄者黄，所入者变，其色也变”，“红者赤，白者白，黄者黄，所入者变，其色也变”等，可以想象当时染色、染布之普遍。如用红色泥土也有染不成功的可能性。另外，这类纺织品的颜色变化在几十年来所发现的战国织物中。下面就以十个战国墓葬发掘资料为主体，将其中发掘出的织物颜色列成表，以彰显当时的流行色。

从此表中得知蓝(蓝)和绿两色在战国时代使用最多，对常用的蓝色是黄色倾向性色系，(如赤)和黑(黑)。红色系中的朱和红根据分析是矿物原料朱砂。绿、蓝、绿两色的见状特征如《诗经》所载蓝草和绿草不易采集的情况相符。朱和黑、红是祭祀用服饰的颜色，出现频繁所当然。黄色系最多则与老化和染黄的染料多种有关。

当时织物颜色的材料常用植物染料之外，还使用朱砂等矿物染料。这些材料分别在下列各种颜色系统中介绍。

一、红色系统
红色系统中有茜草、茶和朱砂。

1. 茜草(Rubia cordifolia, 茜草科)含、情草、茅蒐

茜草是商周时期主要的红色染料，多年生攀援草本。根部主要色素是茜红素和茜素。春、秋两季皆可采集，但秋季挖出的根质量最佳。挖出后剪段后晒干，用时切成片，用热水抽提。色素属酸性染料，不加助染剂只能染黄色。古代用以精炼的植物灰含铝盐，也作为茜素染红的媒染剂。上染后可得茜素染红的黑土湿，可染成红色(棕)。茜草染料染红(棕)和染黑(棕)的色光变化，在史书中，记载最详细，待染色时部分时就再染，守礼法的孔子也将概染部分。原汁或纯染，也就是说不用酸和湿两种染液，染液之间颜色来浸边，装饰衣领、袖、裤。其他红色染料染料还有藻(Polygonum cuspidatum, 藻科)又名虎杖，多年生草本。

2. 朱砂(HgS)

朱砂色泽亮宗，光亮度高。中国境内用朱砂的历史已很久。新石器时代中晚期(约公元前3000-前2000)青海乐都柳湾一具男子下葬有朱砂。安阳殷墟出土的甲骨文片上涂有红色硫化汞，妇好墓出土存有朱砂痕迹的玉柄，荀子(公元前313-前238)器则“朱砂满体，文绣相次”。加之以丹砂(丹砂)。“而秦始皇墓中以丹砂炼成的水银为百川的先例是齐桓公的墓(约葬于公元前562年)”。朱砂有天然的，也有炼成的。制作过程中受温度、浓度和时间的不同会出现多种红色，上层黄，下层白，中间的朱红色。西周偏伯墓群中的朱砂呈朱红色(彩图 X、3)，可见已掌握技术。另外，滇西建筑中的Lemma和儿，凤、虎，其中输出红是用黑色染线和浸渍过硫化汞的红、黑色线线成，硫化汞本身是种晶体结构，多为硫化汞是鲜艳的红色，多为硫化汞则呈深灰色(彩图 X、1)。

二、蓝色系统

1. 蓝草(Polygonum tinctorium, 藻科)薇、马蓝

自然界含蓝的植物很多，《诗经》描述妇女采集的蓝草是其中一种。蓝薇为一年生草本，二年下种，生、六、七月叶长成，呈绿色，即可采叶。采后随新叶，隔三个月又可收割，属柯科原染料，藻色浓艳，颜色非常，朱砂一寸长的留红巾用红秤作猎人的衣服和几只奔跑的动物就是藻红色。此藻红色称肉，后来又称藻、青，之间的色光有无区别，能否因染料不同而引得尚待探讨。

三、绿色系统

1. 茜草(Artchax ton hispidus, 藻本科)录

茜草是一年生草本，茎秆细长，茎叶中含黄色素，主要成分是藻素，为黄酮类染料染料，可直接染毛、丝纤维。以盐酸为染色剂，可得鲜艳的绿色，这或许是其原名绿的原因。

四、黄色系统

黄色系统的染料较多，有上面叙述过的茜草、藻草和缣子。其他黄色染料还有芦(地黄)、姜、黍和䒬等多种植物，是否已被战国时代应用仍待考究，另外还有石黄。
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表1 十个战国时代墓葬所发掘出的织物颜色表。

2. 芍药(参考三、I)也可以直接染黄
3. 栀子(Gardenia Jasminoides Ellis, 花科栀子属)

栀子是常绿灌木，开白花。果实中含有栀子素、果胶、鞣质、藏红花素及藏红花酸等物质，主要的染色分为藏红花酸。用冷水浸泡栀子果实后，煮沸，呈深橙黄色染液，即可直接染得鲜艳的黄色。也可染成嫩黄(铜)、灰色(银)、暗黄(铁)等不同色光。

4. 石黄
据科学分析，巴蜀墓葬中沾有黄色残痕的泥土结果含砷0.1 ~ 0.3 %，未发现铅、锌等金属，而确定为石黄。黄色的天然矿物颜料，分雌黄(AS₂S₂三硫化二砷)和雄黄(二硫化二砷，硫化砷)。腊光似的雌黄呈柠檬黄至桔黄色；脂肪油光的雄黄呈红色18。

五、黑色系统
黑色系中很多染料可以应用铁媒染剂染得，例如茜草染成的红可以媒染成黑。其他还有某些树的果实汁液，也可以媒染成黑。

1. 皂斗，栋树，麻栎(Quercus acutissima)的果实
栋树和麻栎的果实古代称皂斗，是当时主要的黑色植物染料。麻栎(栋、栢、柞)是落叶乔木，高达二十五米。其苞斗及树皮破碎后，用热水抽提，即可染出其中的鞣质(丹宁)，以铁盐媒染得黑。

2. 除了茜草媒，其他可以染皂黑的还有菅(菅菅)，(鼠尾)和揣(乌鸡)等植物。当时表达黑色含义的离有『玄』字，它常与玄冠，玄衣出现。之后又有玄裳、玄衣等语词出现。细则与衣一并出现，是下层贵族礼服。玄、绀色光的
区别同样有待探讨。

上述染草中染红的茜草，染绿的紫草和栀子（地黄）等许多植物，都能直接染得黄色的系色，加上紫色织物老化泛黄、失去光泽，变成褐色，均为黄色系成为统计中最多的因素。

六、紫色系统

1. 紫草（Lithospermum erythrorhizon），紫草科

紫草是多年生草本，八、九月著叶枯萎时采掘紫草根，与棉木灰媒染得紫红色。齐魁公（公在公元前685-前643）好染，全国仿效，使紫色布的价廉五倍于素锦，而招致孩子恶言夺走。曹垣乙迁（约公元前433）出士一具漆衣柜，上则有紫锦之衣，或可反映当时风尚。

七、白色系统

1. 麻灰

麻灰是含有碳酸钙（CaCO₃）的石灰烧成的，可以当精练剂，漂白剂之外，也是白色颜料。江西景德镇出土印有深棕色麻布上的白色颜料，即为新材料。

有关精练部分：

精练是漂白白色染色之前的工作，纤维或布是否精练好，会影响所染颜色的牢固度和光泽。所谓精练就是加入碱溶液，除去除去麻纤维在生长过程中混入的共生物和杂质，使精练解其胶质而呈柔软性，使纤维具有光泽性。《词云》一首春暮歌出士的苎麻布在显微镜观察下“表面光滑，没有胶质，碎屑等杂物”16，而越国生产出的葛布能以“弱于妙经精细”17的词句来形容。这两个例子是证明战国时期植物纤维经过精练。透过《汉书》中的文字得知当时已讲究精练，经过和未经过的织物各有其名称，例如大功麻布和小功麻布都只用水漂洗，捶打，纆先精练，使如丝缕，再煮成布。而读好相反：先织成布后，再加含碱的精练液软化、放松的麻布21。精练可在丝、缕阶段，或在织成布，帛之后再处理，完全依实际使用的需要来决定，通常绢、纨、绢和衣缘的浸边条为未精练物。

麻皮剥下后要经过漂渍、捶打，除去纤维杂质，脱去其胶质，纤维也会变得柔软、纤细。这种利用发酵作用脱胶取得的麻纤维并未完全脱尽其胶质，因此，纤维乃作束联结在一块。要使纤维纤细均匀，还要将麻纤维束劈开分细，即所谓缮麻。

蚕丝是由两根外围包覆丝胶的丝纤维成的。在细丝（用热水煮）时，一部分丝胶溶解在水里，但大部分还是保留下来，这就是未练的生丝。

这种只用水脱去胶质的丝、缕还要精练才能轻柔、富有光泽。按先秦文献有关练丝和练帛的精练制是含有碳酸钾的草木灰22和含有氧化钙的蛎壳灰23，两者均为碱性。练丝用较稀薄的温水浸渍七天之后，白天放在离地一尺的阳光中曝晒、晚上把丝悬挂在井水里，这样经过七天七夜，叫做水练24。

《考工记》中说明，练帛同样用槐树灰汁浸渍（七天），之后，再用鲜树烧成的灰水漆、浸、漂洗、晒干、再浸、漂洗，反复再三，涂碱性溶液和晒干。夜里同样将帛悬挂在井水里。这样经过七天七夜，才完成练帛过程，也称水练25。

至于染色的部分，除了上面提过与染有关的名言外。先秦古书中还有三段叙述织物染色的方法。一处在《尔雅》，说明多次浸染的过程：“一用染之经，再染而经之，三用染之经”26。从第一次用染成黄色的布，再染一次成浅黄色的布，到第三次染成红色的布，这是经过三次染色的方法。这个过程是正色染料的草木多次浸染时染色光色的变化。苟卿述说朱砂涂染羽毛和紫草染料媒染的过程：“仲氏之羽，以朱填丹屏，三月而之，濡而渍之。三人为濡，五人为染，七人为媒。”28

这一段文字的佐证分歧多端，有学者认为《考工记》、《宋书》里有“染”、“染”之名，三为染成红色，再染到第三次染成黄色的涂，他们强调矿物颜料不论触布多少次，色光是不变的。这里从文到后，认为是描述植物染色染色过程。有一派则认为《考工记》是矿物颜料朱砂，朱砂丹砂（红汞）经过水一个月后，丹砂通过蒸发分散成细颗粒的沉淀，用布煮炼，即转化为糊状的粘合剂粘稠。颜料颗粒朱砂即因胶粘剂胶粘在羽毛上，干后形成有颜色的化型膜。著色即成，因此，就有关学者认为染色是三染，三用染料颜料为同一颜色28。陈维凯提出比较合理的看法，他认为这段文字叙述两种不同工艺法，前半段叙述矿物颜料施色法，即石板法，后半段说明媒染现象29，这种解释很合逻辑，解释后文又互相矛盾地方：《考工记》若为植物染料不必要与谷物浸泡、共煮，以为不实。《宋书》即为颜料，是将原三染法染料的色光起变化。

陈维凯说明古代以染染色的媒染过程时认为：混是黑色染料，含硫酸亚铁，在草木灰的黑色水里浸，交又媒染两次后，成青色的染，再染两次成带红色的黑色。他又说近代海南岛黎族把浸过海南岛香树皮叶上的纤维，再用黑木棍浸，染黑染的原料，若浸浸过树叶汁皮，即使草木灰。这种染法的现象，正符合孔子（公元前551-479）强调，意志坚定不受外界影响，深而不薄”的情况。

上述缕丝、练帛和染色是百工中五种设色工中的三种。另外还有绘、绣和缀，后者内容复杂，无从考察。绘画之工在《周礼》中则放在一起说明，绘也色名与四方和天地的关系，以及色彩相生的情况，如，无色、青、赤、白、黄和黑是五等，其意思不属本文讨论范围。同时，发掘出的帛画与服饰功能没有直接关系，因此，绘画不在此讨论。《周礼》也记载染色，蚕以国蚕，青色，黑，黄，紫五彩二色，秋染五彩五色之。另外，还有染草药，草以春秋染草药之，于秋季染五色而给赎人30。《吕氏春秋》中还更仔细地区分了为孟、仲、季三个月，规定仲夏最盛无色染或染色，不准染，不禁止染色，待香风炎炎的季节”命妇官采染，毫不可不为，无从问贵，黑，黄，紫赤不质良，不敢妄作。10
丰富织品色彩的工艺：

战国时代以染料浸染丝、帛以及用颜料透过粘合剂浸渍丝缕、涂布色的工艺之外，还透过织造工艺手段染出的丝帛色彩更生动地呈现出来。从出土的织品中观察到丰富织品色彩的工艺有并丝、织花、绣花和印花等，而印花资料不全，此在不作详述。

一、并丝：

利用两种色泽相近的色丝并合后再织，外观并上便产生一种新的色彩。湖南省博物馆收藏的印地安的纹样是由于黑色和红褐色两种丝线上下交替形的花色，其中红褐色的经线是由一根豆沙色的经线和一根红色纹样丝并合而成的23。

二、织花：

已利用分化布色和改变组织点两种方式来变化色彩。整时经分区分布不同色彩的经线，即能织成不同色彩的纹样。如彩图 X，5 镜衣的边沿所饰黑、黄相间的条纹。纹样纹饰也出现在曾在乙墓出土的编钟架上较大的铜人身上。铜人所著的衣着黑红相间的条纹，另外，运用两种以上的经线或纬线，以改变组织点的方式，使其成为花纹。例如马山西土的田猎纹锦（彩图 X，4）则由深棕经线和深棕、土黄和红棕四种颜色的纬线组成。深黄色的地上以蓝色、红棕和土黄色现花纹，如菱形纹的轮廓是蓝相间，间以穿出于红棕色，花上的猎人著蓝色衣服，黄色腰带，身体的轮廓由红棕色显现。

三、绣花：

用不同色彩的丝线以锁针绣满纹样。江陵马山一号白色素罗绣设计精美的龙、凤、虎纹（N9）和，即所览色谱之丰富：朱红、金黄、银灰、黑。这里所见昂首张口的老虎，身上红、黑条纹相间之红棕色（彩图 X，1），即由矿物颜料硫化汞浸渍而成的其他金黄色为主的有饰花冠，张翅展翼的风和其脚下踏的龙，均以银灰色点出中心，如眼睛、腹和花纹的花托，黑、黄虎的部分同样有四种绣纹（彩图 X，2）：金黄、红棕、黑和灰。最大的区别是老虎的腹部轮廓、张翅的后腿、眼睛、獠牙和鬃毛均用金黄色的明亮色强调出，其他部分的轮廓则以红棕色来表现其阴暗。长尾的尾巴以红棕、黑色两相结合。

总而言之，战国时代已掌握了矿物染色精练丝缕和丝帛，以及烧色的方法，同时，还持续使用矿物颜料粘涂法。此外基本的染染工艺技术之外，还更进一步利用分化布色和改变织造点的织造技术来丰富织品色彩，增加色彩变化，确立了染、织、绣的艺术基础。至于这些颜色名称的源流和染料的关系，以及其出现的先后，一一仍待实验和考究。

注：
1. 《 Çalışke 之陨索引》(香港，1996)，富国篇，页 43。
2. 同上，大略篇，页 126。
3. 4. 《 出境新释》(香港，1963)，篇第，第十七，页 597。
4. 同注 1，劝学篇，页 21。
5. 张绚编著：《墨子集解》(成都，1988)，页 14-15。
6. 影若问楚人纺人与服饰中所得统计类似，见彭浩：《楚人的纺织与服饰》(武汉，1996)，页 211。张政明统计的结果却为红色和绿色，认为为楚人崇尚火赤之风，一致见，张政明：《楚文化志》(武汉，1988)，页 110。
7. 诗九·小雅·采绿：《楚辞采绿》(上海，1886)，页 112。
8. 本文所列染色和矿物颜料的资料多半录自陈维编著：《中国纺织技术史》(北京，1984)一书。同注 3，篇第，第十七，页 597。
9. 同注 1，篇第篇，页 87。
10. 陈新《编者：《中华书局史》(北京，1994)，页 18。
11. 李政：有关西周丝绸之路的重要发现，载:《文物》(1976.6)，页 60-63，页 60。
12. 同注 6，页 34。高汉大教授于 1999 年 3 月底口述说明硫化汞与硫化汞共生，呈灰色。同书，页 33。
13. 同上，页 36。《江陵马山一号楚墓》(北京，1985)，页 104，106。
15. 《韩非子校注》(南京，1982)，页 394。
16. 江西历史博物馆、贵溪县文化馆：江西贵溪岩画发掘简介，载：《文物》(1980.11)，页 1-25，页 30。陈维编于其书中列举很多朱砂涂染的例子，见注 8，页 77。
17. 同注 8，页 76。
18. 同注 18，页 31。
19. 同注 6，页 33。
20. 同注 8，页 71。
21. 同注 6，页 32。
22. 林尹：《周礼今注今译》(北京，1985)，冬官·考工记第六，页 452-453。
23. 同上。
24. 《尔雅注疏索引》(香港，1995)，释器篇，页 71。
25. 上海市纺织科学研究院、丝绸工业宫研究所：《马王堆一号汉墓出土纺织品的研究》(北京，1980)，页 88，页 13，页 451-452。
Lin Chunmei

The Dyeing of Textiles in the Warring States’ Time

The earliest find of textiles in China, dated around 2700 BC is from the Qianshanyang excavation site in the ZheJiang province. But the textile findings which are astonishing in both weaving technique and ornamentation were produced in the Warring States Period (475-221 BC). By this time figured gauges, self-patterned monochrome “damasks” and multi-coloured clothes in warp faced compound were highly specialised. From their rich colours and splendid ornaments we can imagine the fashion of clothes at the time. The dyeing of textiles was not popular in those days. Even the ancient philosophers, after observing the dyeing activity transferred the dyeing phenomenon from the material to an intellectual sphere, for example: “the textile is sturdy white, so it does not become black by dyeing with iron-bearing mud” of “dyeing with green, it becomes green, dyeing with yellow, it becomes yellow”.

This paper will focus on the used colorants and the dyeing of textiles. The excavation reports from tombs of the Warring States Period and written sources before the Han-Dynasty (206 BC - 220 AD) are the base.

Before explaining degumming and dyeing, the fashionable colours for textiles will be listed together with their original traditional terms to give a survey of the then used colorants. The used methods for the colouring of the textiles will be discussed: the first one relates to the application of pigments on the textiles, the second is the dyeing with dyestuffs of plant origin and mordents which will also be described. Finally several arrangements of colours on textiles will be shown. See colour plate X.
古代织染绣品文物的保护技术

摘要
我国各地遗址和墓葬出土的织染绣品文物，品种繁多，色彩绚丽。由于长年的埋藏和自然环境的影响，大部分已经受到严重的污染，对于这些珍贵的文化，必须采取有效的保护方法，才能使它不受继续老化和褪色，保持纺织文物的质地、色彩和纹饰。

出土纺织文物首先应检查纺织纤维原料和染色状况。进行消毒灭菌自理和清洗表面的污垢。对于纺织纤维的麻、棉等，要主要选用碱性的消毒液和清洗剂。动物纤维的蚕丝、羊毛制品，要选择酸性的消毒剂。高温消毒灭菌的温度可选用50-60℃，低温处理的温度在0℃-5℃。根据出土纺织品的状况，清洗后可采取漂洗或蒸洗的措施。清洗时，要制备尼龙网袋和碗筛，用清洁剂要把好小样试验。尽可能保护其质地和色彩的现状。

经清理的纺织文物残片，要进行相同品种、类型的修补加固，可用丝网加固法、玻璃夹持法等措施。大件衣物采用密封保存方法，存放温度虽正常在18-20℃，相对湿度在65%为宜。

纺织品色彩的保护，可用一定厚度的甲基丙稀酸酯类的有机玻璃遮盖紫外光或入射的辐射。同时，可选用有效的抗氧化剂或吸收剂，喷涂纺织品表面或整体铺在玻璃上，达到保护色彩的效果。

中国古代纺织品和衣裳，品种繁多，色彩绚丽。它是人类进入文明社会的重要标志，也是中华民族文化艺术发展的重要表现。郭沫若说：“衣裳是文化的表象，衣裳是思想的形象”。近年来，经考古工作者发掘的遗址和墓葬出土的各种纺织品和衣物，对于民族的繁衍生存、保护自身、美化生活、经济和文化等方面，有着非常重要的作用和地位。它是研究我国民族传统纺织技术进步和精神文化发展的重要历史见证之一。普遍认为我国考古学家和纺织史学家的高度重视，并组织大量人力物力进行研究，过去对于出土的纺织品在纺织原料分类，纺织、印染工艺、花纹图案等方面的研究较多。而对于已经出土的纺织品衣物，怎样进行长期保存、管理？如何防止它进一步霉变、老化和色彩的褪色等保护技术和方法？各国学者都感到困难。还缺乏系统研究。

本文从出土纺织品文物进行妥善保护技术的特殊要求出发，以不损伤或少损伤纸质和保护色彩为原则，就出土实物清理的消毒、清洗方法、入库后的保护技术、管理条件等几个主要方面叙述如下：

一、材质检验
古代纺织品衣物的纺织原料，一般分为植物纤维的麻（葛）、棉和动物纤维的蚕丝、羊毛两大类。通过纺纱、织

绣、染印后，制成衣冠带头等衣物。全国各遗址和墓葬出土的各种纺织品文物，如浙江余姚河姆渡遗址（约7000年）出土的麻布和棉线，河南安阳殷墟新石器时代遗址（距今约5000年）出土的纺、线、浅棕色细麻布和麻布。苏中吴县草鞋山遗址（距今5500年）出土的葛布，长期埋藏在地下几千年，由于各地遗址和墓葬的保存条件不同，周围环境因素的异化。先秦时期的大部分已老化损坏及残片（迹）状。春秋战国时期的墓葬，如江陵马山一号楚墓出土的纺织品文物，保存较少，但受到尸体腐朽的血、油、酸、防、烧、锈、混浊液污染、以及微生物细菌、病毒等的侵害。因此对于出土实物清理中的消毒、清洗的方法和药剂选用，必须根据纺织原料的材质性能和印染颜料的品种特点，选择适当的保护技术。才能基本完善地保护它的质地不受到损伤和引起色彩褪色等影响。

植物纤维中最早使用的植物纤维是葛、葛、麻、麻、苎麻、亚麻等。棉纤维是木棉、草木作为纺织原料。其纤维素结构主要是碳水化合物的单聚葡萄糖，以六元环排列有碳化羟基和葡萄糖键硫键结合而成键式大分子。其分子量较高。如棉纤维分子量可达三百万左右（聚合度为1000-15000），苎麻和亚麻更大，分子量可达五百万左右（聚合度为3000），所以纤维素单键比棉纤维高。由于棉纤维素结构上含有三个羟基，它在酸性水溶液中会发生水解，即引起纤维大分子的键断裂、聚合度下降，强度降低，这种纤维素耐酸不耐碱的特性。在选用消毒、清洗剂时，要注意不用酸液性药剂处理。

动物纤维中蚕丝和羊毛也是我国最早使用的重要的纺织印染原料，主要是以蛋白质分子构成，亦称蛋白纤维。蚕丝是由17种氨基酸组成，其主要氨基酸、丙氨酸、丝氨酸等约为占80%，丝氨酸是丝氨酸和少量的硫，它是耐酸性物质。如果在酸液作用下，会使羧基断裂，产生发蚁，强度下降。羊毛亦是多种氨基酸组成。其中角质素中以精氨酸、丙氨酸、甲硫氨酸、氢氯酸和羧酸的含量较多，还有少量的硫，同样它有酸碱度性质，故用酸液染色。如果在碱液作用下，会使羧基键断裂，产生发蚁，强度下降。因此，在选用蚕丝和羊毛的洗洁剂，去除织物表面的污物时，特别要注意它的酸碱度性质，使织物质地和色彩获得有效的保护。

1972年，湖南长沙马王堆一号汉墓出土大批完好的衣物，主要是金缕木棺的条件，物质呈中性状态，对丝绸织物降低性，它仍有一定的强度，就是妥善保护的例证。古代纺织品衣物在出土时，色彩比较鲜艳，如清洗清洗不当，就会发生较严重的色彩脱落和褪色现象。对于秦汉以前出土的染色和印花织品，首先判定它是哪种类型的颜料品种，是矿物粉末颜料，还是植物色素染料，是否为朱砂、硫黄、石青等，由于它soon织物的予处理后，采用浸染或
涂染等染色工艺，还是稀接夹和后染色、印花工艺。一般将出土的纺织品实物，放置于充满氮气水或无水酒精的容器内浸泡。先去除浮色和表面的污染物。如果是植物色素染料的织绣品衣物，要先脱残片，做局部色的褪色试验，确定它是哪种染料品种（苯、橙、黄、蓝、绿等）。其铲去的方法是在残片上面粘一块滤纸或棉签蘸取，在被试验布料上滴上氨水，看试纸上无无着色反应。如有着色出现，可用2-5%的硫酸或5%的盐酸溶液进行予处理的固色试验。再用显微摄影或电子显色技术，对比其色彩变化情况。但在没有识别它是浮色污染，还是受到某种物理作用下的褪色。这样可以初步确定出土品上的色泽，在清洗前需要进行固色的予处理。对于印金（铜、锡、金、银等）和织物上的片金线，它们一般均使用茂林酸混合金属、或用金箔粘贴在丝面纸的狭条上。由于长期埋葬在地下水中，本身的粘接力很弱，有的已经脱落。如经洗涤，将会造成印刷的花纹，剥落殆尽，失去原有金色光彩。因此，出土印织物的纺织原料、染料和加工方法的初测检验，它是文物保护很重要的措施和先决条件。

二、除尘消毒

纺织品文物出土后，先要检查实物残片的变化和清洗程度。对大块、大件的保存较好的文物衣物，可用木屑等除去表面尘土。再用吸尘器吸取器皿中的尘土杂物，由于墓葬中随葬的纺织品衣物，一般都带有细菌病毒，又受到地下各种微生物侵蚀，必须进行灭菌消毒处理，以防止危害人体健康。常用的消毒处理方法是化学药品消毒与高温消毒。

化学药品的消毒方法是，将取出器皿的纺织物，用丝线或棉布垫层包好，放入消毒剂熏蒸内，放入配置好的一定量消毒药品。已使用的有乙烯醇、甲基硫、四氯化碳等，还有用环氧乙烷（C₂H₄O）和二氧化氯混合溶液。进行熏蒸，放入密封性好的房间内，放置时间3-5天，以保证文物上残留的病毒、细菌、微生物等有害物质，彻底清除。

高温消毒灭菌方法有蒸汽法、远红外法和微波法等。蒸汽消毒是将文物包覆后放入蒸汽箱中，温度一般掌握在50-60℃。因有细菌、真菌在高温蒸气40℃以上时，8小时内可杀死，如果温度过高，会使文物发脆、散裂，褪色，要注重其变质情况。远红外线和微波辐射是利用高温热源效应新灭菌消毒方法。在印染行业中，有远红外烘机机新设备，可以将大件的文物放入远红外烘机箱中进行，温度可控制在60℃左右，时间较短，亦可达到高温灭菌效果。微波加热消毒灭菌法是比远红外法更为快速，效果更好的方法。它可根据出土文物的品种状况，利用电磁波产生的热效应，迅速定温温控灭菌消毒，不会损坏文物质地和色泽。

在现场国内的现代化博物馆，按计划对馆藏的衣物定期进行处理。尤其是精品、珍贵衣物的陈列展示，研究文物保管，非常安全可靠。此外，低温消毒法也可以因地制宜，是经济实用的无污染的常用消毒法。纺织衣物上附着的虫卵、细菌，一般在0-15℃低温条件下，便会死亡。如我国东北地区，最低气温可达零下30℃以下，平均气温在零度以下的5-6个月，可直接将纺织品衣物置于低温冷冻的条件下，消毒和保管。在其它季节，亦可用冰箱、冰柜进行冷冻处理。

阳离子灭菌消毒是近年来研制的杀灭新方法。其作用原理是根据细菌的细胞壁和细胞膜由磷酸酯双分子膜组成，呈负电性的性质。按物理学中异性电荷相吸引原理，将加入阳离子消毒剂，使其涂抹的细胞壁会被阳离子的正电荷所吸引，从而束缚细菌的活动自由度，抑制其呼吸机能，并促使细胞壁和膜结构变形、破裂，细菌迅速死亡。

据研制的阳离子表面活性杀菌剂介绍，用1:1000浓度的水溶液，在半分钟内能杀死金黄色葡萄球菌、绿脓杆菌、大肠杆菌和霉菌等有害菌，产品对纺织品衣物，毛巾的保护，可以有效喷洒于纺织表面，就能达到操作简便，保持原貌，且无污染的良好效果。

三、清洗方法

出土的纺织品衣物经消毒处理后，必须有针对性的进行清洁处理。出土的衣物，一部分是遗址墓地的随葬品，一部分是在棺内穿着在尸体身上的，受到较严重的污染。如衣物随葬品在沙墓干燥和高寒地区，不在棺内出土，表面无严重的溃烂污物，一般可用干洗处理。对于棺内混杂的衣物，采用干洗，能解决口感的血肉、脂肪、病菌等腐败物而造成较大块面的溃烂顽迹，必须进行重点的清洗。要根据出土衣物的情况，如能用干法洗涤的，就少用或不用湿洗法为原则。以达到清除污染，保护文物的目的。

干洗法的采用，要根据出土衣物的保存程度和清洗条件而定。如厚型织物（丝绸、绒、缎、锦、织金错绣等）薄膜的渍染未渗入内部，且污染面积较小，或多种彩色印刷织物，可选用挥发性强的溶液状干洗剂。如丙酮、三氯乙烯、四氯乙烯、石油醚等。对于一般性染污（浸渍状污）局部浸染，可用乙烯、丙酮、乙酸、乙酸乙酯等溶液干洗剂。用毛笔或毛刷蘸取溶液擦拭，再吸水吸干，或用布擦拭，然后用吸水吸干的布擦拭。直到除净干净，最后用丝绒柔软剂1%和醋酸稀释溶液5%配成混合液喷洒保护。

湿洗法是用于棺内出土、纺织品表面浸水的衣物、血渍等污染的清洗顽迹。面积较大，异味难闻，以及轻薄的纱罗织物。印染衣物，要配置专用洗涤溶液。要准备好清洁浴（挤衣、衣架或不锈钢编织篮），还要配备一定规格的平网滚筒筛（不锈钢筛网）作载体，分配好筛网。筛网大小、重量配制的品种、面积而定。如清洗厚型织物的，大件衣物、裙、裤等，可选用30-50目筛网。轻薄型织物，小面积和破损衣物，可用60-100目的筛网。在清洗时，使污物可顺利通过筛孔沉淀于筛底。

洗涤剂的选用，要以不影响出土文物变质和褪色为前提。过去曾用中性皂片，现在有去污力强的丝毛混合型洗涤剂。其组合成分有乙醇、乙酸、乙酸乙酯、丙酮、乙酸乙酯溶液等以及丝毛等柔型洗涤剂和蒸馏水等混合，清洗处理的方法和步骤是：先将需清洗的污染衣物平展置于水网上，放入
洗涤液中浸渍，对于污渍严重的，可在液中存放 1-2 小时，甚至更长时间，使洗涤液浸透到纱线内层，再用毛巾在表面衣物清洗干净，不留污渍为止。最后用蒸馏水，多次冲洗。使衣物上残留的洗涤液。取出后在室内干燥，如太阳光照晒会引起衣物干裂和褪色。或用温湿毛巾调自控熨斗整理，去除污渍表面皱纹叠状，保持衣物原有的平整状态。

四、修复加固

出土的纺织品衣物，由于在遗址和墓葬的部位和条件的不同，有的自碳化破损为残片，有的残结在青铜器表面，有的和泥土凝固在一起，经清理消毒、洗出后，大部分呈多块分离状的残片，先要辨识它的品种质地。色彩、花纹的特点，进行同件、同类种类组织花纹的归集拼接工作。用丝绸在织物背面加固，以避免品名在编号造册过程中。对于厚重织物的织锦残片拼接修补，使用尼龙丝网加强固，轻纱纱罗，可用高目数的尼龙丝网，或用南京博物院研制的一粒单丝按经纬向粘结的蚕丝丝网加固。经加固后，仍保持原有柔软性和光泽。有利于研究分析和保存原貌。

喷跋防波树脂法，是丝绸残片和丝绸老化福发的衣物，已使用的加固法的方法之一。在丝绸表面喷加酸性乙烯或尼龙浆增加强度。如 1956 年故宫定陵墓出土的丝绸丝织物，表面喷后，现在完全失去了丝绸丝织物的丝绸光泽、柔软性和弹性，已经变成硬发皱的丝绸标准了。丝绸翻动时会掉下粉末。在国外还有一种少传丝绸破损的保存法就是浸渍在稀释溶液，如毛利登试用丙烯树脂和水性溶剂醇醇醚树脂，据说介绍有此方法处理古代文物残片，织物纤维的原有柔软特性不会丧失，色泽几乎没有变化，反而比原来的鲜亮（色泽的本质没有变化，因为树脂溶液渗入织物，原未织物内外粘结的尘埃脱落，实际上是进行一种清洗作用）。然而，微妙的一点是织物本质失去了，例如丝绸的纤维强度无法知道。染色加工过程中附加的还原剂，染料剂也分不清了，于是失去了探索加工方法的资料，丝绸的风格也变了。因而树脂加固的方法，还要继续进行研究。

玻璃壶柄法是丝绸常用的保存方法。过去的一般方法是用两块平玻璃把残片夹起来，用胶带在四周粘贴起来。这种方法能达到简易目的。但是，几乎全部的残片在平玻璃中有水分凝结起来。这种方法能达到简易目的。但是，几乎全部的残片在平玻璃中有水分凝结起来，有时候，玻璃碎了，丝绸残片会粘在玻璃上拿不下来，不去在玻璃上的残片会通过玻璃之间滑动，水分凝结，可能是由于残片本身不干燥，也可能是后来收集的环境温度变化引起的。如果密封的玻璃之间隔开了水气，而一般的玻璃是石英玻璃，玻璃中的碱会溶解出来而使残片损坏。

平玻璃夹残片时，要带一块白布纱布，这样有一面是与玻璃隔开的，剥离时会容易些。网对丝绸的磨损系数大，而且残片不会在玻璃板之间滑动。美国纽约美育罗普利堂美术馆博物馆织染品保管部长葛宜女士收藏的一系列染色织物，用了两种不同的夹玻璃的方法。过了四十年，再去进行比较，用的埃及第十一王朝时代（公元前 2500

年左右）的麻布（长二米到三十米，宽一米半），在布上用同单宁酸和铁的混合液写上字，做纸造模的标记，或者用同样溶液染的麻麻织成的布，在 1940 年剪下十厘米见方的几块，分别夹在玻璃板里，那块麻布，不论是在展示过程上还是收藏过程中，都是暴露在空气中的。特别是折叠（按出土时状态）的外侧，强度很弱，容易碎，而保存在玻璃板里的状况就比较好，布的颜色和当时夹入玻璃中时一样的洗净清洁，完全没有碎成粉末的危险。丹宁酸和铁染色的那部分，发现时因氧化已发黑。由于玻璃板的保护，发掘之后又经过了四十年，仍旧经得住摄取操作，并保持着纤维的较好状态。

五、贮存保护

在古墓葬保存条件好的纺织品和衣物，由于长期浸泡在水里或棉里，它的物理机械性能和弹性都会降低。一般用上法先除去杂质和气味，再使织物保持干燥，以防止膨胀及霉变。日本目部顺义教授介绍朝鲜东陵汉墓的法是把丝绸放在水里保存。当丝绸放在水里，溶于水中的氧气会和蚕丝作用，但等到这部分氧气消耗完了，水便隔绝空气的作用，这和丝绸埋葬于地下浸泡在水里的条件相似。我国在南方的地方出土的丝绸品，如湖北江陵马山一号墓，湖南长沙马王堆汉墓、江苏金坛东汉、福建福州黄中侯墓等，均因受上述条件的水封特点，所以丝织品和衣物就完整地保存下来。

古代丝织品最合适的保存条件是一个重要的探索课题。尤其是象长沙马王堆汉墓和福建黄中侯墓出土大批的丝织品和整件的服饰，所占面积大，不能用玻璃夹法等来进行技术保护。这些珍贵的丝织品和大件的服饰，有的要作科学研究，有的要作常期保存在库内。研究、展览和展览往往是交替进行，保存技术也随着情况而变化。因此，日本的学者为保存正仓院和各寺庙内的丝织品，曾组织专门力量研究丝织品保存的主要条件。如湿度、温度、光线、温度和空气等，对收藏在库内的丝织品变化情况。他们采用的保护方法主要是密封。正仓院的丝织品每年开关两次，组织展览和科学研究。他们发现日本弥生时代，密封的箱柜内的丝织品保存状态是很好的。他们会将出土的丝织品密封起来，放在地下温度变化不大的地方。保存效果则更好。根据我国马王堆一号汉墓出土的丝织品和服饰，他们保存在具有成分的条件，这，个汉墓的墓穴，随葬品保存的条件是深埋和完全密封。这墓的木椁四周围和上部填充了三十到四十厘米的木灰，它的外面又封固了六十到一百二十厘米的白膏泥，水和气体都从外面侵入。棺椁又深埋在地面二十六米，完全密封，不受地面温湿度的影响。虽然在埋葬时大气温度可能很高，由于白膏泥的密封，墓室中的湿气被周围大量的木炭（约一万斤）吸收直到一定程度，使墓室内部的湿度。温度（是摄氏 13-14 度）始终保持不变。棺内放置随葬品，里面没有空隙，裹尸布的丝麻织品又浸泡在箱灰内。所以棺内丝麻织品的颜色非常鲜艳，质地也很好。出土的丝织品就不能造成这种密封的保
存条件。台南博物馆将马王堆汉墓出土的丝织品，用塑料袋中封真空充气，放入木箱内，再放入木柜内。柜内用空调装置，保持一定的温度。湿度，使丝织品和服饰的保存条件，在类似密封而不受外界温湿度条件的影响状态下，已保存20余年了。根据博物馆的黄启聪教授的丝织品，用木箱装好，再放入木柜内，木柜内控制温湿度，均收到很好地保存效果。

美国的博物馆和文物保护研究的学者，也都探索条件的温湿度保存条件。如日本正仓院的土段部林氏提供资料。1949年在十年里，对正仓院的气候调查结果。考虑正仓院里温度外温度变化。冬天因不热，而室温保持在15℃左右。对正仓院内的温度和湿度有调节作用。而正仓院外的温度变化。在正仓院内，温湿度变化的幅度是很少的，正仓院内也有一定。日本专家的意见也不一致，甚至认为温度尽可能低，相对湿度50-60%；室温保持在23℃，相对湿度为60%以下为宜；室温保持在30%以下。相对湿度75%为宜。相对湿度以60%为宜的根据是：在60%以上空气中的水分与空气中的氮起作用，它会促使纤维吸湿。同时会产生局部湿度。室温保持在60%以下，会使纤维很快吸湿。故以50%为宜。

美国西德罗普利艺术品保存的相对温湿度为50%。美国家木博物馆在正仓院的月度为45-55℃，相对湿度为50%。这是当时的温湿度条件，可能与所保存的丝织品和丝绸的保存条件有关。目前，对整个大块丝织品的保存条件并没有肯定的结论。

1970年，为纪念日本万古博物馆，也为了后代人知道现在人的生活，由每日新闻社和松下电器公司主办，用特制的钢板高大，内有多间介绍日本现代文化特点的物品和记录。把两个时代保存资料的重叠地摆在地上展示。资料的内容凡有209项，其中包括各种纤维制品，与丝有关的蚕桑曲（日本、中国、东南亚的织品或纤维），有如丝（15厘米的丝），日本（天然染染成淡蓝色），大岛、结岛、本组染、博多织、长广、山泽、本色织、木都等，有各色丝质的织物卷成小径放于资料柜，再用不锈钢板做成的小箱装起来，放在资料柜上的一部分。丝织品在密封前先抽成真空，再灌入干燥的空气，使它的内部为一个大气压的气体情况。丝织品的保存在上面的资料柜，由2000年开始，以后每二年一次检查一次，每月检查一次，检查一次后变化。对于那一点，一定到在五千年前。即690年，才能启封查考。保管的湿度温湿度是17.5℃，资料柜内有大窖保持这样的温湿度。丝织品在柜子里的保存是把在空气洁净的室内进行，同时充分的杀菌处理。丝织品在保存时，要和空气隔绝，不能和空气中的湿度相接。丝织品通过这种密封保存，按上述年代开启取样试验，可以比较科学地系统地掌握织物保存的情况。对于出土纺织品文物的保护技术研究是有积极作用的。

两个丝织品的保存条件于1971年1月20日（No1）和1月28日（No2）埋在大阪城内木丸，到了1971年3月15日，EXPO’70开幕周年纪念日举行竣工仪式，同时移交日本文化部管理。根据日本文部省的预测，丝织品在内收藏的丝织品，包括染色的，五千年大概不会有变化。

六、色彩保护

丝织品的染色、印花和刺绣品的鲜艳色泽的色问题，亦是纺织文物保护的课题问题之一。日本染料工业研究会研究认为，氨、氯、氧的空气对丝织染料影响较大，受光的影响较大是染料系，其次受酸性染料，对染料染色影响较小，而光氧化物的氧化物的影响。在丝织品展出时，可能用酸氧化物的有机玻璃，如果用透明聚酯，这样可看到染色的色泽，说明空气中的氧化和染色光影响更大。

关于丝织品的保护方法，美国美罗普利艺术馆保存方法是：用五百多米合成聚酯板为内层，以聚氯乙烯乙烯的破坏作用。丝织品合成聚酯板的材料是甲苯氰酸铝（俗称有机玻璃）。根据试验，它能遮蔽90-99%的紫外线。这是保护丝织物和染色的色泽的重要性质。该馆美术馆使用的紫外线吸收型有机玻璃是德国公司出品的UF3 Acrylith，厚度为1/8英寸。和英国汉森公司出品的UF4 Acrylith，正面无色或颜色很淡，能很好地遮蔽丝织品。同时能防止紫外线引起的染色现象。根据日本JISK7614飞机用有机玻璃试验，当厚度为2.5毫米（0.25英寸）时，波长在290-330纳米范围内紫外线。其透过率为50%以上。日本的试验研究表明，无色有机玻璃如果不能遮蔽紫外线，它的透射光率从2500A开始就能透，加上正常的紫外线防护剂后，波长在3500A以上有光可以透过。它不吸收可见光，可见光的透射率约93%（表面反射率为7%）。3毫米厚的有机玻璃Acrylith，对2500-3000A的紫外线透射率为20%。若用同样的厚度，紫外线吸收型有机玻璃，却只吸收0.5%。紫外线波长范围是130A-3907A之间。日本正仓院的丝织品保存，是将防紫外线的有机玻璃夹片，做成大或小的量筒，装入丝织品的纸箱或木箱里，放在空气中不流通的暗处。可随时随地可见，十分方便。但是这种保存方法不能看到反面。对于丝织品，只能看到表面，这种保存方法可带来研究观察的不便。

丝绸的色泽变质，染料的褪色，主要是紫外线照射和热两个因素引起的降解过程。美国S.P.Hersh等研究认为：丝绸受到紫外线照射氧化，引起染料分子结构发生变化，导致了丝绸色泽发生变化。以深色的蓝色现象最明显，而热则使染料变黄。紫外线光照射对纤维变色的影响相当大，光氧化使纤维变色程度降低。对于出土纺织品文物的保护，尤其在博物馆陈列展览，研究保管，显得特别重要。于是，研究使用抗氧化紫外线光吸收剂，对衣物进行保护的实验，正在深人地开展。因为抗氧化紫外线光吸收剂，能有效的吸收紫外线，并将其光能量转变成无害的热能形式而消散。国外几种主要的抗紫外线光吸收剂是：

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UV-531，其2-羟基-4-正辛氧基二苯甲酮，为浅黄色结晶粉末，溶于乙醇、丙酮，挥发性低，低毒，能吸收300-375nm的紫外线。6-二羟基一基对甲酯，简称BHT，为白色或浅黄色粉末或片状物，溶于乙醇、丙酮、醋酸乙酯等溶剂，无毒、无味。它是应用较广的非活性抗氧剂，能够有效地抑制空氧化和热降解等。苯并三氮唑，简称BTA，为无色或淡黄色晶状结晶物，可溶于水、乙醇等。其酸性溶液不够稳定，但碱性溶液稳定性良好，在高温时可分解出苯胺、硝基苯等有毒化合物，味苦，有微刺激性。BTA由瑞士Ciba-Geigy公司首先，是目前国际上比较好的抗氧化紫外线吸收剂，可有效吸收300-400nm的紫外线，稳定性高。它已在青铜器、铁器保护方面应用效果较好，中国的张雪莲在研究丝绸的抗氧化紫外线吸收剂保护作用及对比试验后，也证明了BTA对丝绸防老有较好的效果。同时她首次提出用天然芦荟叶萃取为白色粉末状固体，它易溶于水及有机溶剂，无毒、无味、无污染，使用方便。芦荟素主要是蒽醌衍生物和芦荟苷类的苦味酸酯和石油醚，它有湿润、保湿、抗氧化的特点，是优良的光稳定剂。芦荟和苯并三氮唑（BTA），UV-531等抗氧剂，在出土的丝绸残片上作老化褪色测试，对比其白度变化证实芦荟和BTA具有同样的抗氧
化吸收紫外线的作用，能将有害的紫外光能吸收，转变为无害的热能释放掉。因此，天然芦荟是较好的抗氧化剂和热稳定剂，对防止丝织品和颜料色彩保护，具有明显的效果，对出土纺织品文物的陈列展示、贮存保管，提供了新的途径。

结语

通过以上古代纺织品衣物几种处理方法和保护技术的叙述，对于中国历代织染物的质地、色、纹的保护技术，在收集、保护、展览时怎样防止其继续老化和变色等复杂问题的研究，已经取得重要的进展。但纺织品文物保护技术的方法，有其特殊性，必须接受较长时间的考验。它有待于各地文博部门和文物保护技术的学者们的共同努力，不断总结已有的保护技术经验，积极研究推行之有效的科学保护方法。才能使历代多姿多彩的纺织品文物长期地保存下去，流传于世。为光辉的古代文物遗产的保存和展示，科学技术史、文化艺术史的研究和发展，提供最珍贵的可靠的物证。

注：
1. 湖南省博物馆：《长沙马王堆一号汉墓》上卷，文物出版社，1973年。
2. 湖南博物院：《长沙马王堆一号汉墓出土丝绸品研究》，文物出版社，1980年。
3. 上海博物馆：《中国丝绸》，文物出版社，1982年。
4. 上海艺术博物馆：《中国丝绸》，文物出版社，1982年。
5. 布料原色：《染织品的保存法》，《古文艺术的科学》，第3号，1952年，第21-26页。
6. 李恩：《染织品的保存法》，《古文艺术的科学》，第5号，1953-54号。
7. 王志义：《丝绸工艺》，《古文艺术的科学》，第6号，1954-55号。
8. 顾铁符：《论长沙汉墓的保存条件》，考古，1972年第6期，第53-58页。
9. 榴 glands：《染织品保存法》(12)，第57页，第157-177页。
10. 日本正仓院事务所保存科科长阿部弘氏的信，1977年5月9日：喜多村一男：《正仓院之气象》，大安区气象台，1960年，第23-25页。
The textile and embroidered relics excavated from the ruins and tombs all over China are varied and often coloured. Most of them are broken fragments and some have been seriously damaged due to their long stay underground. Effective protective methods and techniques have to be adopted to protect these valuable relics from further decay, aging and fading and to maintain their texture, colour and patterns.

The first thing to do when conserving textiles is to examine the dyeing conditions of the raw textile fibre material, then sterilise the material and finally clean the surface to remove the dirt. Alkaline disinfectant needs to be used to clean flax and cotton fabrics of plant fibres while acid disinfectant needs to be used to clean silk and wool of animal fibres. 50 - 60°C is the right temperature for high-temperature disinfection while 0 - 15°C is suggested for low-temperature treatment. Whether to use a dry-cleaning or wet-cleaning technique must be determined by the condition of the unearthed woven and embroidered fabrics. Before washing, nylon racks and washing grooves should be prepared and a small sample test should be made before deciding on the cleaning agent. A priority is to keep the texture and the colour intact.

The cleaned textile fragments should be repaired and reinforced by using measures such as silk-screen strengthening, glass clip holding, etc. Large pieces of clothings are to be kept separately and sealed off. The best temperature for silk and satin storage is 18 - 20°C and the suitable relative humidity is 65%.

To protect the colour of textiles and embroideries an organic glass of methacrylate ester in the right thickness should be set up to keep out ultraviolet light, which causes fading. In the meantime, an effective anti-oxidation ultraviolet absorbent may be sprayed on the fabrics or the protective glass to protect the colour of the exhibits.
中国先秦衣装颜料色彩与文化

中国是世界文明古国，礼仪之邦，衣冠带履，锦绣天下。我国大地物博，色彩资源极其丰富，色彩文化积淀深厚。在古代对“色彩”、“采色”、“縉色”之称谓。“采”是指矿物颜料的天然颜色，“采”是指植物(动物)质素的原有采色。“縉”是指丝帛染印的仕上色泽。这两者既有物系上的区别，又有应用上的统一。我国的先秦衣装与美、审美的原始色彩观念出发，是最早发现和使用矿物颜料彩陶、染衣裳民族的一种。对于古代色彩名物的定义、分类以及光色和物体色的基本现象原理的认识，已有三千余年的历史。“未用之采，已用之采”《尚书·正义》引注，未用之采是自然固有之色，已用之采则是人工(制作)之采，这便阐明了“色”与“彩”的内在联系和辨证关系。

中国色彩名物的起源与发展，在大体上经历了原始社会的“三彩”(赤、黄、黑)，夏商周时期形成的五色“(青、赤、黄、白、黑)，秦汉时期的七彩(赤、绿、黄、青、蓝、紫、白)唐末以后的“九色”(赤、橙、黄、绿、蓝、紫、白)四个阶段。本文根据考古发现的器物色彩实物资料，通过纪年材料的记载，现就先秦色彩的主体色彩名物的两大类型，使用彩绘、涂抹、浸染、束带、印模等工艺技术，呈现出衣物(器)上的萌芽，成长，壮大和拓展的发展过程作些探讨，并从彩陶文化、青铜器文化和丝绸锦绣文化等方面，说明古代的色彩名物在中国文明发展史上的作用和地位。

色彩是存在于自然界天地万物中固有的质素。它是人类认识自然本质的直观表现之一，也是最早用来表达原始审美意识观念的重要标志，远古先民们认识色彩，应用色彩历史悠久，从旧石器时代原始部落民族已有了色彩的审美观念。北京周口店山顶洞人遗址(距今约2万年)，考古学家发现遗骨下用一层红色粉末铺垫，经鉴定，它是赤磷的赭石(Fe₂O₃)，赭石粉末就是最早的红色颜料实物。同时，山顶洞人用赭石粉末涂在空心的小骨棒，骨器，骨角，牙骨，黑陶光等空白上绘画或涂绘，在手镯上，有装黑饰纹。以此，可以推测彼时的彩绘是被涂上赭色颜料。这种涂饰着色的行为，意味着原始染色技术的萌芽，它们亦是原始先民们最早以色彩表达审美意识的物证。

在仰韶文化时期的新石器时代发现的彩陶，最具彩陶文化的色彩性。如陕西西安半坡遗址(公元前4115±100年)的彩陶上有用赭红，黄，黑三种颜色烧制的人首(戴帽)虫身，鱼纹网状动物。作为氏族的标志一图腾(totem)。青海省大通县上孙家寨新石器时期遗址(公元前3300年)出土的“三组"五女携手舞蹈"彩陶盆子上亦有赭、黄、黑三种色彩。陕西宝鸡北首岭遗址(公元前5850-前5400年)发现随葬条状或小块的赭红、黄色颜料石和粉末，浙江余姚河姆渡遗址(公元前5000年)出土了涂朱红色的漆器，双凤朝阳纹样的菱形器，似蛋纹雕刻的小鸟等装饰品，临江山前家岭文化遗址(公元前3000年)早期出土的整套彩陶陶器(轮)，有其重要的纺织文化特征，先在陶纺轮两面涂朱黄陶衣，再在细面涂赤红色的同心圆纹，漩涡纹，三角纹，弧线纹等。第一次发现的薄胎(黄泥质)晕彩陶瓶类器物，它是灰、黑、红成黄色的陶衣上，用黑色彩绘出菱形、网格、圆条、锥状等纹饰，富有无级层次的晕彩效果。确是五千年前的色彩艺术精品！河南郑州大河村遗址(公元前3790年)出土的彩陶以衣(嵌入)器壁上彩绘以部分为特征，如红黑色、红色或褐红色彩绘，浅淡灰色和白色陶衣，制成太阳纹、网状纹、鱼尾纹、弧线纹等纹饰。

色彩颜料的制备和使用，制陶器在新石器时代中期已有实证可考。如甘肃兰州东郊白道观遗址属马家窑文化期的祭祀场，发现了5座12座陶窑，其中有一个资料坑。内有制造陶器的原料和陶器，并出土有研磨颜料的石板和棒，以及磨制颜料的陶罐，陶罐分格，中配紫红色颜料。秦岭临潼姜寨遗址(公元前4600-前4400年)出土的彩陶上还绘有乌、黑、绿、蓝色彩纹，还有黑色颜料黑锰矿石(MnO₂)散块和粉末。同时出土的一套彩绘工具由有石砧(臼)、磨泥板、磨棒、灰陶水罐、在砚凹和捣粗中有残留的黑颜料共五件，它是我国发现最早的配套研磨颜料和彩绘黄色的工具。此外，江苏镇江大墩子遗址(公元前4500年±105年)发现一赤铁矿石小块表面有研磨痕迹，石板、石片上附着朱红色粉末。山西夏县西阴村遗址(属仰韶文化期)中发现一个下凹石臼和破断石砧，表面上附有朱红色粉末。这一系列的考古发现的颜料，并非孤证，足以说明原始氏族先民已认识到利用铁矿石粉末，石黄的风化物，以及锰黑石粉粒，经石粉，石棒等简单研磨工具，制彩陶用的所用的矿物颜料细粒度的事实。

关于布彩制品上的着色，衣装上的涂色的问题，曾有学者推测他们先民们用色料涂身上(手)的延伸，逐步发展成为现代的美化装饰，为织物涂染色的起源获得了启示，即将原始纹身的审美习俗移植到织物(带刺)的美化衣装。这亦是原始生产者们最早以色彩表达审美意识的物证。

在仰韶文化时期的前一阶段新石器时代发现的彩陶，最具彩陶文化的色彩性。如陕西西安半坡遗址(公元前4115±100年)的彩陶上有用赭红，黄，黑三种颜色烧制的人首(戴帽)虫身，鱼纹网状动物。作为氏族的标志一图腾(totem)。青海省大通县上孙家寨新石器时期遗址(公元前3300年)出土的"三组"五女携手舞蹈"彩陶盘子上亦有赭、黄、黑三种色彩。陕西宝鸡北首岭遗址(公元前5850-前5400年)发现随葬条状或小块的赭红、黄色颜料石和粉末，浙江余姚河姆渡遗址(公元前5000年)出土了涂朱红色的漆器，双凤朝阳纹样的菱形器，似蛋纹雕刻的小鸟等装饰品，临江山前家岭文化遗址(公元前3000年)早期出土的整套彩陶陶器(轮)，有其重要的纺织文化特征，先在陶纺轮两面涂朱黄陶衣，再在细面涂赤红色的同心圆纹，漩涡纹，三角纹，弧线纹等。第一次发现的薄胎(黄泥质)晕彩陶瓶类器物，它是灰、黑、红成黄色的陶衣上，用黑色彩绘出菱形、网格、圆条、锥状等纹饰，富有无级层次的晕彩效果。确是五千年前的色彩艺术精品！河南郑州大河村遗址(公元前3790年)出土的彩陶以衣(嵌入)器壁上彩绘以部分为特征，如红黑色、红色或褐红色彩绘，浅淡灰色和白色陶衣，制成太阳纹、网状纹、鱼尾纹、弧线纹等纹饰。

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程度来看，可能是长期浸没在地下，表面的粗粒子剥蚀，色彩就淡而浅了。但锦纹丝之间附着明显的碳红色，足以证明它是经过涂染加工的第一块染色织物。

夏代以前彩陶文化中的“三彩”赤、黄、黑原始色彩观念是怎样形成的？为什么红（赤色）又是人类最先使用的色彩呢？这可能是原始部落先民存在一元的神灵崇拜的信仰问题。在中国新石器时代的大汶口型（彩陶、岩画等）上装饰陶器划着“+、Ω、○、×”等纹饰。这是日神（太阳神）符号的象征。太阳代表着光明和生命，氏族先民首先见到的朝霞的红太阳和赤色太阳的自然现象，其次才是红色血液的象征，生命不息，子子孙孙繁衍。再其次红为给人温暖、醒目、刺激的感觉（如红日、火、光、鲜花等），依据中外许多学者的调查考察，红是由于人类一开始使用图纹、纹身的第五保护色。传说有善神、恶鬼、护身符的作用，因此，赤红色是上古氏族普遍崇敬的色彩，并采集易得的红土制红陶礼器和工具，并使用赤铁矿粉末涂染红色织物，纹身和保护美化生活。

夏商周时期，农牧业、手工业等有了一定的发展，手工业中的陶器、冶铜、制陶等生产技艺上出现了较大的进步，用于器物装饰的色彩品种不断扩大。颜色由新石器时代的“三彩”（赤、黄、黑）扩展为“五色”（青、赤、黄、白、黑）并应用于衣料上。《尚书·虞书》记载，传说帝舜令夏禹做衣裳的故事：“予欲观古人之象，日、月、星辰、山、龙、华虫（彩雉）作会（画绘）；宗彝、藻、火、粉米、黼、黻画绣。以五彩彰施于五色作服（裳）。”这种章服制度规定前六章上衣花纹是用彩绘彩色经线，后六章下的上衣花纹是用彩线刺绣加工的。《周礼·考工记》载：“画绘之事，五采备，谓之绣。”“绣绘之工，共职也。”《礼记》“衣画而裳绣，有五色。”这里的“五彩”是指青、赤、黄、白、黑，是第五种彩绘经线、彩绣的颜色。夏商时代，由于朝廷提倡耕织经济，蚕桑丝绸印染手工行业得到较大发展，商代朝廷设“女桑”、“土桑”官，专职负责蚕桑。丝绸印染产品的征集和生产、珍贵的丝绸，绚丽的色彩，官府王室对衣裳和装饰品等需用量大增。据《考工·轻重》载：“昔者燕（商代燕国）之时，女乐三万人，倡操未正，闻于三衢，是无不服文采衣裳者。伊尹以薄之游友文绣，纂组一纯，得粟百钟于桀之国。”《帝王世纪》载：“商纣多发美女，以充后宫之室，妇女称王三万人。”(《帝王世纪·帝今本》，1964年版)。《说苑·反质》引墨子对禽滑羔说：“纣为鹿台渔猎，酒池肉林，宫墙文采，锦绣被堂，金玉珍宝，妇女优倡，钟鼓管弦，靡靡不至，……非惟锦绣绮丽之用也耳。”可见，在夏商时代，色彩丰富的锦绣装饰织品，单是供王室贵族达到惊人的程度。另一面则说明了，黄色色彩品种增加，丝帛染色工艺得到了相当的发展。

商代对于青赤黄白黑五色现象的认识，周“五色”观念的形成，已有三千余年的历史。在殷墟的甲骨文中发现青、赤、黄、黑、白的名称。《说文·象形》以文来扭组。如熊熊燃烧的炎炎发出赤色光，随着火焰温度的变化，火的光色会变成黄色光，白色光，青色光，最后残留灰黑色。火的光色现象与现代色度学中的光谱色相原理的加法混合律是基本一致的。甲骨文“五色”是：“赤色，大火之炎也。赤者为火之炎。甲骨文中有‘@’，‘@’，‘@’，‘@’，‘@’。”

青色，火的光色之一。青的古文为“青”，甲骨文中有“青”，“青”，“青”等象形字。《说文》：“青，东方之色，从丹从日。”

白色，火的光色之一。白的古文为“@”，甲骨文中有“@”，“@”等象形字。《说文》：“白，东方象，日光火，从日。”

黑色，火的光色之一。黑的古文为“@”，甲骨文中有“@”，“@”等象形字。《说文》：“黑，东方色，火从日。”
一种白色颜色是数据灰（即水煮粉状）。《周礼·注疏》：“祭礼共器之器”。汉郑司农注：“器可以直器，令色白。”周代掌握礼器的官府，负责采集烧制的器皿作白色颜色，并在容器上饰有白灰色。

赤色颜料是朱砂。亦名丹砂（硫化汞HgS），色为朱红色。在历代，由“祭献”管理的重要赤色颜料。商代出土的丝织物中用赤色颜料朱砂涂染的织物较多，如北京商代宫殿遗址所出商代玉器，正反两面均有涂有朱砂和麻布痕迹。织物表面往往带有赤色朱砂。河南安阳殷墟妇好墓出土的丝织品有朱红色，均是经朱红色染的。陕西岐山虢家村西周早期墓出土的丝缕残片，均有涂染朱砂颜色的痕迹。陕西宝鸡茹家庄西周墓出土的卷草纹绞饰铜器残片，有涂染朱红色，仍非常鲜艳。

关于赤色颜料中的朱砂颗粒的细度问题，是否已具备织物和朱砂颜料的条件呢？北京平谷刘家河商代墓出土的朱砂，使用显微镜观察了朱砂颗粒的大小，如下表1：

<table>
<thead>
<tr>
<th>颗粒直径</th>
<th>30微米以上</th>
<th>10-30微米</th>
<th>5-10微米</th>
<th>3-5微米</th>
<th>3微米以下</th>
<th>很多</th>
</tr>
</thead>
<tbody>
<tr>
<td>数</td>
<td>0</td>
<td>14</td>
<td>54</td>
<td>120</td>
<td>11</td>
<td></td>
</tr>
</tbody>
</table>

Tab. 1. Particle size of cinnabar pigments.

注：此表摘自《中国纺织科学技术史》古代部分，科学出版社，1984年。

上表中所列朱砂微颗粒经研磨精制在3-5微米以下的超细粉末，就可用于丝织、绣的朱砂染色。在古籍中记载的“朱砂”、“朱粉”，可能是指未朱砂的朱红色。又如商代原始石器的“朱砂”，后世称为“朱砂”，因色泽如朝霞状红色而得名。它亦是未朱砂所染的朱红色丝织品。由于丝织物所染的朱红色，因其色泽鲜艳，以后被用以染色。《诗经·正：》“朱衣不纯”。后来，朱衣带成了囚犯的标识衣裳了。

黄色颜料是石黄的粉末，石黄为雌黄（As₂S₃）和雄黄（As₂S₃）两种，雌黄黄色较纯，雄黄为土黄色，陕西宝鸡茹家庄在西周墓出土的丝缕残片，有赤黄色带黄色颜色。其中黄色为雌黄石黄所染。由于石黄黄色纯正，耐光性好，是常用的黄色颜料。

黑色颜料是黑石（辉铋）粉末，常用于陶器制作。在服饰上的用黑丝，亦称炭色。由于“兽尚白，鸟尚赤”的习俗，周代及以下设有“掌黑”的官职，因松香烟色而有光，一般在衣服上很少使用黑色颜料。在春秋战国墓出土的丝织物上，使用黑色的丝织品是非常少的，有的黑色是用（植物）皂斗黑色素染成的黑色所代替。

殷商时代以青铜文化为特征，发展起来的青白石黑五彩色彩。它普遍用于织绣衣物和彩陶器等器物的镶嵌，做彩，以供王室享用。商代王室崇尚的色彩，以“素白”为尊贵色。《诗经·礼记·文王》：“夏后氏尚玄，殷人尚白，周人尚赤。”有些论著对于“殷人尚白”，多用“五行相胜”的说法来解释。其实，“殷人尚白”，以白色为贵，白色为贵的色彩崇尚习俗，由来已久。首先，殷人尚白是由对太阳崇拜而引发心理上的特征反映。殷人的祖先就是东方炎帝炎帝，原始对太阳崇拜的习俗。太阳是光明的象征，给氏族带来幸

福生活。先民直观太阳光是白色的进形成以白色为尊，为贵重的观念和习俗。在殷墟卜辞中记载对太阳的祭祀名目繁多，有“日、月、及、桓、吾、御”等（《殷墟卜辞研究》），科技1，第3-4页。又据郭沫若先生说：“殷人在日之出入时有祭祀……盈朝夕礼之”。(《殷墟卜辞编纂释文》)，第354页。相传东夷族祖先有太岁，少岁（吴），又称“吴”，是取其光明之义，是先民对太阳崇拜之字义，字形上的体现。传说中的白帝少吴氏是光明之神、阳光的管理神，后人称为白帝，穿白衣，白虎纹，掌管方西，中央天象色。

其次，殷商以白色为吉祥、从事各种活动，传说成汤时，连续七年大旱，汤以身祷于桑林，雨。“汤之救也，驱承车白马，大帛布衣，要白茅，以身为质。”《尸子》的记载，留下了商代“尚白为吉”的色彩倾向。殷人作战时驾白马，并“戎事乘羊，用白玉”，称为“白之大吉”(《礼记·明堂位》)。殷代的车用木料制成，不用彩色装点，故称为“素车”(《礼记·礼器》)。殷商最贵重的器物是青铜器，除此外是白陶，白陶是用高岭土烧制，色泽洁白，素净细密，专供王室使用。殷商遗址墓地出土的白陶器，虽然有较多使用的遗物。还有出土许多白色玉器与白玉首饰器物陪葬品，这些都说“殷人以白为吉”的民俗文化。

再次，“殷人尚白”表现在庆典、祭祀等礼仪活动时，均以白色为贵。殷商王朝对轻软洁白的玉器丝织、丝绸，当作是国计民生的大事。《史记·殷本记》：“帝纣伐西，伊陟为相，有高宗；成汤之臣，共丁战斗。”朝廷专设“女桑”、“士”等官职，从事管理蚕桑丝绸业生产。又据《礼记·礼器》记载，有“桑神”、“蚕神”，称“桑神”，祈求雪白蚕丝丰收。在殷墟出土的甲骨文字中，祭祀蚕神有11块。如殷王武丁卜辞中：戊子卜，王幸蚕，九。”(《甲骨合编》7402)说明朝廷呼人省察蚕事，占卜次数至少有九次之多。殷王祖庚、祖甲卜辞中说：“蚕示三日”。八。《合集》承报说：“示示”即“蚕神”，“父”为一耕牛，羊羊羊羊之名。这是说在八月祭祀神，用三公之母的羊羊六牲，祭“蚕神”仪式，非常隆重。卜辞中还有“蚕王”之名。“蚕神”和“王”，被臣民赋予最高的尊崇(《殷墟书契前编》六·六七)。殷人视蚕为天圣，是“蚕神”所赐洁白光亮的蚕丝丝织，给人们带来最高贵的用料。甲骨文辞中的“桑”字一般公认的24字，如果“桑”字表示方国名，地名(产地)，以及“丧”字的借假字计有二百余见，《甲骨文字释林》，上卷，第75页)。卜辞中的字(、)等，计从字书字形81个，从从字的字16个，从结字的字3个，共有100字。如果将有“丝”旁有有关的象形字数量在150个以上。可见，殷商王朝对于蚕桑丝绸生产的倡导，王室贵族们对丝绸贪婪的享用，达到了十分惊人的程度。它更增加了“殷人尚白”的崇敬心理。丝绸品种和生产工艺，均得到了较高的发展。

从殷商时期出土的丝织品残迹，如殷墟妇好墓，大司空墓。河北藁城台西村遗址，北京琉璃河燕国都遗址等贵族墓葬中的实物品种，如纨、纱、绮、素、绮等均为白色为本色丝织品、衣裳、巾、褐、履、旗等物品，也是以白色为流。并有色彩(朱红、浅绿、土黄等)的纯、绣、织带、组、纲、腰部作为装
饰。殷人以白色为贵，希望吉祥，祭祀礼仪，常以白色作为礼服。这种丝绸（丝织绸缎）饰物，披麻戴孝（孝），的“殷人尚白”的习俗，一直流传于后世。

三
西周初年周公姬旦辅佐成王后，朝廷对王室、官吏的便服、黑（礼）大衣、规定了色彩、花纹、质料和缝制工艺相结合的“九章衣制”。据《尚书·虞书》：“以五采彰施于五色作服（衣裳）。”《左传·昭公二十五年》：“衣裳之文，九文，五采，五章、左、右各五色。《礼记·玉藻》：‘五章即采异色’。《礼仪·内乐》：‘衣裳之章文异色’。《礼仪·月令》：‘女命妇之冠（女冠）简采采而文（文）’等官职。以保证 thoại衣料的供应。又据《考工记》载：衣物上的彩色上色，有“设色之工），即：“画、绣、钟、镂、镂”为五种普通使用的文彩装饰材料。其后经《周礼》中礼仪的规定，生产染衣料的彩色材料。这种以植物（草木）染料进行染色加工的“青、黄、赤、白、黑”五色丝绸，无疑为周代染色技术发展的最大成就之一。而且在染色的品种、数量上也达到了相当规模。使用染丝色彩更加多姿多彩。它在世界的色彩文化发展中确立了十分重要的地位。现在根据《释名》、《周礼》、《礼记》、《考工记》、《尔雅》、《左传》等先秦著作，以及各地诸侯贵族（楚墓）出土的丝织品与衣物上所反映的彩色实物，按植物染料的“五色”序列于下：

蓝草，染青蓝。它是一年生草本，六、七月间，蓝草叶呈绿色，即可采收，采集后新鲜叶，隔三个月又可再收割。用鲜叶发酵，氧化综合成靛酸（C6H4N2O2），是靛酸还原原料。《诗经·小雅》：“终朝采蓝，不盈一筐。”《礼记·月令》：“仲夏令民毋采蓝以染。”蓝草有多种，这里是指蓼蓝，为布帛普遍使用的青蓝色染料植物。天然靛蓝（C6H4N2O2），因其成分中含有 20% 的靛红素，尚有少量的酸棕素及黄色素存在，故色泽是带红光的蓝色。至于《易经》、《坤卦》中的“天玄而地黄”、《周礼》中的“玄衣涂裳”、“玄冕”等中的玄色，应是天空色或天蓝色。因这种玄色，当时还不能用靛蓝染得，故称玄色，是玄幻莫测之意。万里无云，看到的是天空的天蓝色（天）。直到战国时荀况《劝学》中说：“青取之于蓝而胜于蓝”名句，才说明有了真蓝色。这就是在靛蓝染色中欲抑红存青，染色时浓度和碱还原的浓度过高，才能除去酸棕素，得纯靛蓝青的青色效果。东汉《说文》中的“玄”是“黑而有赤色”。也不能误为黑色（《丝绸研究》1994, 1期）。

染草染绛，草草，又名仇草、茹蓝、茅芜。《诗经·郑风》：“绮服如朝，车马之衣。”《诗经·大雅》：“采蓝文布，可以染绛。”注：一名蓝，今之鞫也，染绛。（《尔雅》注）它是多年生草本，春秋季采挖其根，切碎，用热水提取
“五色”和“五方”相结合的“五方正色”，最早见于《周礼·冬官·国匠》：“有方之事，采五物。东方谓之青，南方谓之赤，西方谓之白，北方谓之黑，天地之玄，地谓之黄”。这些先秦史实的史学概念，与《国语》所称的“阴阳五行学说”的倡导，又将“五方”与“五色”五行、四时、五帝、五方、金、木、水、火、土等组合联系，构成了复杂的衣装制度上分为等级的彩色体系。使“五色”成为观念赋予了社会意识形态的形象。它对色彩概念的扩展，丝织文化艺术系统化，均产生了深远的影响。

青色是东方，春天、草木萌发的象征色，青色是东方的方位色，又是天空色。表示着东方破晓时的黎明色，鱼肚白，又转为天蓝色，即青色中含赤色的蔚蓝色，天青色是秋夜时的天空色，又称空色、碧色。《释名·采帛》：青，生也。象物生时色也。春天，草木青青，绿意盎然，满园春色。相传五帝之一的帝喾（明亮之意）氏，着青衣（青色纹），掌管四方，春天。神旗句芒辅佐帝喾的草木萌生。又夏为赤色，赤为火色，而号为赤帝。

赤色是南方，夏天、火的象征色。赤色是南方的方位色。表示着南方，夏天。赤色炎炎，骄阳似火，它是典型的暖色调。相传炎帝神农氏（又称太阳神），着朱衣（朱雀纹），掌管南方，夏天。火神祝融辅佐，负责五谷繁育，万户紫气生。又夏为赤色，色赤为周灭夏，火克金。

黄色是中央方，四季、土的象征色。土在“五行”中占有中央地位的方位色。《诗经·小雅》：“土，中央，生万物者也。”相传五帝之首—黄帝轩辕氏居在黄河中游的中心。土呈黄色。黄帝有四个面孔，率领四方，四季。着黄色黄巾（龙纹）衣。土神后土辅佐，负责稼穑万物，供衣食。黄帝为土德色黄，因此，古人将土地黄色视为帝王色。黄色是黄色中明度最高的色，又有大黄色，明黄色，汉代以后，成为帝王衣的专用色泽。

白色是西方，秋天、金（金属）的象征色。《诗经·小雅》：“白，西方，万物既生之始也”。西方是日落之方。秋天草木成熟，收割，给人以凋谢没落之感。金，表示镰刀和兵器，故有“杀气”的含义。相传白帝少昊氏，穿白衣（白虎纹），掌管西方，秋天。白神蓐收辅佐，负责收割庄稼。《礼记·月令》：“孟秋之月，白露降，寒风至，万物白敛”。以白色象征秋天，而称之为素秋。白色是先秦表示衰悼的颜色，制白衣，素裹是祭祀、尽孝的用。

黑色是北方，冬天、水的象征色。北方，冬天，冬天意味着寒冷。黑色是黑色，颜色正是冷色调。《释名·采帛》：“黑也。如晦明（夜色）也。相传帝喾后稷氏，穿黑衣（玄武纹），掌管北方，冬天。水神玄冥辅佐。但水并非“黑”，常用白山（白山），“黑水”作形容词，可能北方冬天，水和雪映照下去似乎变成了“黑”了。正如黑龙江是远看的色泽。又秦代为水色，色尚黑，秦灭周，统一六国，水成黑。《周易·乾卦》1988年1期）。

周代衣装制度有正色与间色的尊卑之分11。《礼记·玉藻》疏：“正色，间色色，天子、公、候、大夫、伯者在祭祀、上朝会客、外出等场合，衣装（冠服）的色彩有严格规定：如玄冠朱衣（天子之冠）也，编冠编经诸侯之冠也，编冠玄武之帽之冠也。《礼记·玉藻》1988年1期）。

1115五色正色是由五方正色中每两色相配混合而成，如现代色彩学中的“二次色”正色和间色的关系可组成“五方色环”或“五角星形”分布图。示中的分布色是：青色为间，色为红，青色为间，色为黄，青色为间，色为白，青色为间，色为紫，青色为间，色为绿，间色为红，间色为绿，间色为红，间色为绿。
水德胜火德。易服色制度，‘衣裳龍服衣服皆上黑’。秦尚黑，黑色是‘五正色’之尊，大礼服用之。但常服的颜色仍五彩缤纷。矿物颜料用于衣裳彩绘（包括兵马俑、宫廷装饰等），和植物染料用于衣物的染色、印花、生产规模扩大，需求量多。印染技术发展很快。西汉初期朝廷专设‘今史、织史、三服官’，有职员工数以万计，为皇宫和官吏衣装服务。《汉书地理志》：‘齐三服官作工种数万，一岁费数万万’。‘长安东西织室亦五万室’，官府织入丝织业人数多，耗资大，不惜工本，追求色彩艳丽的织锦。刺绣等高级工艺品，推动织锦印染技艺的全面发展。《史记货殖列传》载：‘千家衣裳，其人与千户侯等’。丹朱砂等经营者，一年可获利二十万金。汉代初期用于衣裳的彩绘、染色、印花的矿物、植物颜料品种日益增加。矿物颜料有朱砂、丹砂、石黄、石青、孔雀绿、胡粉、服白、服云母、金、银等。植物染料种类繁多。有黄檗、黄栌、茜草、蓝草、紫草、郁金、龟头、松烟等。丝织品的浸染、染色、套染的色谱丰富，绘画、套印印花也相应发展。1972年湖南长沙马王堆一号汉墓出土的丝织品各种衣物一百余件，保存完好的衣服有袍服、夹衣、裙、手巾、带等 58 件。丝织品有刺绣、编织、绸、缎、绒等。经过鉴定，用植物染料的蓝草、蓝草、钟子、紫草等色素，进行直接染、染色、套染的原色、间色、复色，以及深浅、浓淡的不同明度和彩度的颜色有 20 余种。其中以红色色谱为主有朱砂、红、丹砂、深棕、深红、紫红、暗红、黑等色彩（《江陵马山一号楚墓》，附录一，丝织品色彩测定，文物出版社，1985年）。

四

秦始皇统一六国后，根据吕不韦的‘五德相胜’说：秦灭周是
<table>
<thead>
<tr>
<th>织物名称</th>
<th>经纬线</th>
<th>报告中的色名</th>
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<td>YR3</td>
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<td>纬线</td>
<td>深棕</td>
<td>YR3</td>
</tr>
<tr>
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<td>A、B、C、D、E型大菱形纹锦</td>
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<td>YR3</td>
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<td>土黄</td>
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<td>YR3</td>
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<td>土黄</td>
<td>YR3</td>
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<td></td>
<td>经线</td>
<td>深红</td>
<td>YR3</td>
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<td>纬线</td>
<td>深棕</td>
<td>YR3</td>
</tr>
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<td>YR3</td>
</tr>
<tr>
<td></td>
<td>经线</td>
<td>棕</td>
<td>RO4</td>
</tr>
</tbody>
</table>

Tab. 3. Colours of the yarns.

表3. 织物的经纬线色彩对照表

以上大量出土的丝织品衣物的色彩，有力地佐证了周代的流行色是以朱红色调为主，此即史载“周人尚赤”的实物依据。它和各种黄色、蓝、灰黑色等色彩线相匹配、协调，织锦、刺绣或几何纹、花卉纹、龙凤纹、舞人动物纹等纹饰，制作的各式衣袖、帽、履，更显得多姿多彩，再现战国时期的色彩文化艺术风貌。
Fig. 3a, b. Silk painting (details), Western Han (206 BC-24 AD), 1972 excavated in grave No. 1 at Mawangdui near Changsha, Hunan

图 3a. 长沙马王堆一号汉墓出土彩绘非衣 (帛画), 上部; b. 中部。
印花敷彩纱锦袍，是首次发现的印花和敷彩相结合的产品。花纹是藤本植物的菱形纹样，整个印刷分为七道工序。第一是印出藤蔓灰色底纹，即用阳纹版印单元纹样，高为 40 毫米，宽 22 毫米的菱形骨格，第二用朱红色绘出红花；第三、四、五、六是用灰色点花，黑灰相间黄（深黄色）；银灰相间加深，棕红相间花纹。第七是用粉白相间增加和加点，印花敷彩纱锦所用颜料，经实验证明用发射光谱仪，硫化物定性分析，X 射线衍射仪鉴定分析，朱红色为碳，白色是铬云母，灰色是硫化铅和硫化汞的混合物（图 4, 5, 6）。

![Image](image-0x0-to-552x831)

Tab. 4. Powder X-ray diffraction from cinnabar silk No. 460-1.

图 4. 460-1 长寿绣袍上朱红绣线 X 射线衍射强度谱图。

| 表 4. 出土丝织品 460-1 上朱红颜料与硫化汞的 X 射线衍射强度比较表 |
|---|---|---|---|
| 峰线序号 | 460-1 长寿绣袍上朱红色颜料 |  | 六方晶体标准硫化汞 |
|  | 晶面间距 d(Å) | 相对强度 (I/I₀) | 晶面间距 d(Å) | 相对强度 (I/I₀) |
| 1 | 3.62 | 5 | 3.59 | 5 |
| 2 | 3.36 | 100 | 3.359 | 100 |
| 3 | 3.16 | 26 | 3.165 | 28 |
| 4 | 2.87 | 97 | 2.863 | 94 |
| 5 | 2.37 | 6 | 2.375 | 9 |
| 6 | 2.07 | 26 | 2.074 | 26 |
| 7 | 2.03 | 9 | 2.026 | 12 |
| 8 | 1.98 | 23 | 1.98 | 29 |
| 9 | 1.90 | 4 | 1.90 | 3 |
| 10 | 1.767 | 15 | 1.765 | 21 |
| 11 | 1.735 | 15 | 1.735 | 27 |
| 12 | 1.682 | 15 | 1.679 | 25 |
| 13 | 1.586 | 5 | 1.583 | 5 |
| 14 | 1.564 | 5 | 1.562 | 6 |
| 备注 | 试验电压：40 千伏 | 试验电流：20 毫安 | 扫描速度：1/2°分 | 扫描范围：5°-60°(20°) |
表 5.461 上银灰色颜料与硫化铅、硫化汞标准数据的衍射强度比较表
注：vss 最强 vs 极强 ms 次强 s 强 m 中 w 弱 mw 次弱 vw 极弱

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<tr>
<th>序号</th>
<th>461-银灰色涂料</th>
<th>硫化铅 (ASTMS-0592)</th>
<th>硫化汞 (ASTM 卡片 6-0256)</th>
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<td>1</td>
<td>3.43 vs</td>
<td>3.429 84</td>
<td>3.359 100</td>
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<td>3.16 w</td>
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<td>2.95 vvs</td>
<td>2.969 100</td>
<td>2.863 94</td>
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<td>4</td>
<td>2.86 m</td>
<td>2.10 s</td>
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<td>2.10 w</td>
<td>1.98</td>
<td>2.074 26</td>
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表 6.461 上白色颜料与白云母标准数据的衍射强度比较表

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<td>17</td>
</tr>
<tr>
<td>14</td>
<td>1.50</td>
<td>w</td>
<td>1.499</td>
<td>40</td>
</tr>
</tbody>
</table>
The Dye Colours and Culture on Clothing in Early Qin

In the early Qin Dynasty woven and embroidered clothes were dyed by using such techniques as dye application, dip-dyeing, mordant dyeing, printing, etc. Great headway was made in the technology. The 5000-year-old light crimson silk gauze unearthed from the ruins of the Qingtai Village of Henan Province is a good example of the dyed fabrics in China. Of the three colours (red, yellow and black) in the Painted-Pottery Culture, the most individualistic colour used by the primitive tribes on their utensils was amber.

Over three thousand years ago in the Bronze Culture of the Xia and the Shang Dynasties, people began to recognise the 5 colours of mineral dyes (green, red, yellow, white, black). The 5 colours originate from the five colours, which are shown in the colour combination of the inscriptions on bones and tortoise shells at that time. Ground dye powders such as cinnabar, azurite, stone yellow, black stone, lead white etc. were used to dye fabrics into brilliant clothes. The fact that people of the Yin Dynasty cherished white shows that they worshipped the sun and regarded white as auspicious.

The Official Robes of the Zhou Dynasty stipulate that colour is one of the indications of rank and nobility. The court had 5 different craftsmen (Hua, Hui, Zhong, Kuang and Huang) in charge of making coloured silk robes. Plant dyes like madder, blue grass, jasmine, purple grass etc. developed quickly. The then used techniques such as dip-dyeing, mordant dyeing and expanding the spectrum. The five principal colours and their tints advocated by the scholars of Yin and Yang during the Warring States Period not only refer to the 5 colours (blue, red, yellow, white and black) but also refer to the 10 tints (green, crimson, blueish green, violet, Liu Yellow, yuan, reddish black, light yellow, grey and greenish black), hence the Chinese idiom “five colours and ten tints” which means brilliantly colourful. People in the Zhou Dynasty adored red colour and regarded “red” as noble, which is testified by lots of unearthed embroi- deries of the Spring and Autumn Period. See colour plate XI.
汉魏云锦中的五色

汉晋杂记中多见五色云锦或五色锦之名，这里的五色或五彩毕竟是是指专门的五种色彩，还是仅仅泛指多种色彩；它与中国传统文化中的五行、五方和五味等是否有直接的关系？在《礼记》中多见“五色、布、丝、缕、火、地”等名。这两书均传为晋人所著，书中记载多有差异。但同时肯定的是书中提及的物名，一般者是当时存在的，因此，这两条记载还是汉魏时期丝绸名目客观的反映。考之于出土丝绸实物，可知所谓的云锦就是指云气动物纹样为主题的丝绸。因此在汉代统治者十分敬奉于道教和巫术的神学说，他们登太山封禅，建仙阁灵宫，在各种艺术作品中画云气，饰之为云气。因此，在丝绸织物中具体的装饰则是大量的云气纹及与云气相伴的各种动物纹，正如山大韩嘉祥山汉画像石铭文所说：交龙立蛇，猛虎延逝，玄猿登高，狮熊践道，众禽群集，万兽云云。同时，在云气动物纹间，织纹大量出现吉祥的词语，如“延年益寿大安占”、“长寿明光”等，它们往往成为我们对某一丝绸的称呼。

稍有的《论语》中记载赵武玉乘丝锦中生产的丝绸有：“大登高，小登高，大明光，小明光，大博山，小博山，大茱萸，小茱萸，大交龙，小交龙，蒲葵文锦，斑文锦，凤鸟朱雀锦，锦绣锦，桃钱文锦，或青绮，或白绮，或绿绮，或紫绮，或绿绮，工巧百数，不可记名。”书中提到的各种锦名也可以看出新疆出土的云气动物纹丝绸相吻合，其中关于色彩的记载更是引人注目，其记载有青、白、黄、绿，紫五种色名，色名之后的锦在此应作解地，也就是说，在公元三、四世纪，新疆丝绸的常用色彩中一般有以上五种。

五色或五彩在先秦及汉代文献中十分常见，《礼记》中多见“五色、布、丝、缕、火、地”等名。这两书均传为晋人所著，书中记载多有差异。但同时肯定的是书中提及的物名，一般者是当时存在的，因此，这两条记载还是汉魏时期丝绸名目客观的反映。考之于出土丝绸实物，可知所谓的云锦就是指云气动物纹样为主题的丝绸。因此在汉代统治者十分敬奉于道教和巫术的神学说，他们登太山封禅，建仙阁灵宫，在各种艺术作品中画云气，饰之为云气。因此，在丝绸织物中具体的装饰则是大量的云气纹及与云气相伴的各种动物纹，正如山大韩嘉祥山汉画像石铭文所说：交龙立蛇，猛虎延逝，玄猿登高，狮熊践道，众禽群集，万兽云云。同时，在云气动物纹间，织纹大量出现吉祥的词语，如“延年益寿大安占”、“长寿明光”等，它们往往成为我们对某一丝绸的称呼。

二、古考发现的五彩云气动物纹锦

汉魏时期的丝绸无一例外地采用平纹经二重组织。所谓的平纹经二重组织是用夹纬将多种色彩的经线分成表里两层，表层的经线就是显示在织物正面的色彩，而其余的经线则沉在织物下层。当织物需要另一种色彩的经线时，则将此经线提升到表面显示，而其余的经线沉到下面。平纹则为经圆与经线的交织规律。

在一种组织中，表层经线与沉在里层的经线线之比是一个重要的因素。并非经二重就是表里层各一种经线，表里各一是它在表里经比为1：1时的特例，但也可以是1：2、1：3，甚至是1：4。在某一特定的区域中，不同色彩的经线数数是由表里经线之和，也就是说，当组织表里经线比为1：2时，色彩数应为3，当表里经线比为1：3时，色彩数应为4。但必须指出的是，这里的色彩数只是局部区域中的色彩数，并不代表整幅织物的色彩数。在汉锦中常见的现象是，将不同色彩的经线按不同区域排列，织物因此而呈现色彩条效果。这样，尽管在某一局部区域中有着一定的色彩数，但在整个组织中的色彩数总数是等于或大于这数。因此，在此文中，我们所称的五色丝绸组织实际上是指整幅内色彩总数有五种的组织，而将表示某一局部的色彩特征用比例来表示，如表里经线比为1：1的经组织组织为二经锦，以表示在同一组织中由二种色彩的经线为一组，表里经线比为1：2的经重二经为三经锦，1：3的为四经锦，依次类推。

从新疆出土的汉魏时期丝绸来看，色彩数少于五色的丝绸不多。若有的话，一般却是二色锦、二色锦由于其正反面的组织相同，图案上恰恰是相反。如新疆楼兰遗址出土的续
世锦，以蓝黄两色纸纹和“庆世锦”三字，一面是蓝色天地，另一面则为蓝色地。最新从新疆尼雅遗址出土的风格相同。纹样一为“世国锦宜贵亲之孙”纹样的也是蓝黄二色，效果与之相同。再件楼兰出土的纹样亦同为蓝黄两色。三色和四色纹样非常少，所知者如新疆尼雅遗址出土的阳字纹和楼兰出土的蓝纹锦，鱼纹锦，均不属云气动物纹。

事实上，绝大部分的云气动物纹样都是五色锦，但根据组织和使用不同的，可以将其分成几类。

1. 三经五色锦
三经锦在织物的每一区域都用三种经线为一组进行表里换层而显花。但在不同的区域中用不同色彩的经线，这样的区域在每一幅中往往有十余个。在每一个区域，三种色彩一般是地色，地色和地色，不同区域间的色彩和经线色往往相同，只是更被主体色而已。大部分的云气动物纹样均用三种色彩进行交替花，形成保二换三（保证三种色彩)，另三种色彩进行替换）的规律。以下是一组实例：

a. 延年益寿大吉之孙锦：这类锦织出土最多，不仅在中原有出，而且在俄罗斯也有出。但最为有名是新疆民丰尼雅古墓中出的用此锦制成的刀鞘和手杖。从色彩上看，它属于早期的纹状花，红色为地，白色为经，另一种色彩是用黄、绿和棕三种色交替花；

b. 万世如意锦：新疆民丰尼雅古墓出土，作为锦的重要的面，在红地为地，白色为经，红色为经，白色为经，绿色和红色相互替换作为不同地区中的主体色。从纹样上看，也是早期的纹状花。

c. 还有少数的三经锦发现，如楼兰出土的“延年益寿”锦和“长命百岁”锦等，从图上分类均属于纹状花。由于它比较残破，在残片中只发现四种色彩，但我们推测它们在色彩总数上也应该是五色锦。

2. 四经五色锦
四经锦用四种色的经线为一组进行表里换层而显花。但在不同的区域中用不同色彩的经线，四种色彩一般是地色和经色，另两种色为地色，另两种色为地色，另两种色为地色和经色，而往往相同，只是更被其中地色主体色而已。但只用两种色彩交替替换，形成保三换二（保证三种色彩)。另二种色彩进行替换）的规律。以下是一组实例：

a. 登高明望四海富为国庆锦：出自新疆楼兰，以深蓝作地，红白夹经，三种色彩作为主体色，其中色在各色区均相同，还可有绿和黄作为主体色，形成保三换二（保证三种色彩，另二种色彩进行替换)的规律。

b. 永昌锦：同出新疆楼兰，以深蓝作地，白色为经，红色为不变主体地，另两种色和浅黄和白色作主体地。织物上残留永昌”两字；

c. 献锦：出自新疆楼兰，已非常残破，但还可以看到完整的纹样，深蓝作地，浅黄作经，红色作不变主体地，绿和浅黄(黄)作主体经色。织物上残留“永昌”两字；

d. 王侯合千秋万岁宜子孙锦：新疆尼雅三号墓出土，以小单元的带有纹状特征的云气为主体纹样，并由左至右织入“王侯合千秋万岁宜子孙”纹样，织物为深蓝为地，红、白、黄色经，绿、墨色作作为变换出现的主体色。

在图上，彩锦不图云气动物纹样，但其色彩风格则非常相似。现在发现有三种，一件出自新疆楼兰，以红色为地，白色为经，鲜艳的蓝色为不变主体色，另两种色彩为绿色和黄色；另一件出自新疆尼雅三号墓，以白色为地，深蓝作经，红色为不变主体色，绿色和黄色为变。从图上，彩锦是五经锦中的云气动物纹样均属云状花式，理论上的出现较晚，彩样稍晚。特别是登高明锦一件，从纹样上就可看出与山墙有关，并与巫丧礼制相联系。在生产的锦纹“大登高”和“小登高”相吻合。

3. 五经五色锦
几乎所有的五经锦均属云状花式，云气动物纹样。五经锦在每一区域中均有五色色彩的经线里换层而显花，本身就是五色。再查之于其色彩，均无区域，整个幅面内均为同一色区，也就是说，这些所发现的五经锦同时也是五色锦。

a. 长乐光明锦：出自新疆楼兰，深蓝色，浅黄色(黄)为经，白色为经，白色为经，白色为经，绿色和棕黄色为主体经。通体不变，主体色不同，有“长乐光明”四年菱形花；

b. 长寿光明锦：同出新疆楼兰，深蓝色，浅黄色(黄)为经，白色为经，白色为经，白色为经，绿色和棕黄色为主体经。通体有向下的浅黄色经线显花，形成条纹状，色彩独特，有“长寿光明”四年菱形花；

c. 金池凤锦：原物为小彩状花，出自新疆尼雅一号墓，按研究其图案可以拼复成为对称的彩状花，还可以看到纹样和花卉，残存“金池凤”三字。白色作地，蓝色为经，其它色为黄、绿和绿色；

d. 五里出东方中国锦：原物为中国一彩锦，出自新疆尼雅二号墓，图案不同分色区域，均以黄、绿、黄、红、白五色织出，以蓝作地，白色作字，白色和红色在云纹的左二经花；

三、云锦五色与五行的关系

从以上我们对新疆等地出土的汉魏时期云气动物纹色彩的考察来看，当时除一些与云气动物纹靠近或非常简单的外图形之外，大部分云气动物纹的用色总数恰好都是五色。如云锦在同区域中只能用三种色彩的经线，织锦就通过不同色彩的经线区排列来增加两种色彩；如果锦只能用四种色彩，织锦就再增加一种；五经锦已达五色，也就不再分色区分。由我看来，这一现象同既自然，它应与当时的阴阳五行学说相合。

五是中国古代一个非常特殊的数字，许多场合都对五行有专门的定义。如上所述的五行吉、木、火、土与五方东、南、西、北、中是其基本的含义。此外我们还可以看到有五音、宫、商、角、徵、羽；五行或五行，君臣、父子、兄弟、朋友，五五或五种兵器，五行或五种礼节，五谷或五种食物，五金或五种金属，五更或人体的
The Five Colours in Polychrome Silks with Cloud Pattern from Han Dynasty to Wei Period

Based on the analysis of all available specimens of polychrome silks with cloud pattern from the Han dynasty to the Wei period (actually, from the 1st to the 4th century AD), an interesting phenomenon was found. Almost every piece of silk was composed of five colours, namely dark blue, green, yellow, red and white. This also applied to polychrome silks with 1:2, 1:3 and 1:4 warp-faced compound structure. In addition, Han dynasty documents contain references to wuxing jin (silks with five colours) and wuxing yunjin (silks with cloud pattern in five colours). This suggests that the five colours on polychrome silks have a special relationship to the wuxing (five materials, which are metal, wood, water, fire and earth) and wufang (five directions or locations, which are east, west, south, north and the centre) in Chinese philosophy because each direction and each kind of material is also associated with a special colour.

One important example which strongly supports this hypothesis is a polychrome silk recently discovered in Xinjiang. It bears an inscription of Chinese characters, wuxing chu dongfang li zhongguo zhu nanzhang (it is a favourable time for the central country to conquer the southern Qiang tribe when the five planets appear together in the east). This piece consists of warps with five different colours, each symbolising one of the wuxing (five planets): jin (Venus), mu (Jupiter), shui (Mercury), huo (Mars), and tu (Saturn), which have the same names as the wuxing (five materials) in Chinese. See colour plate XII.
Late Antique and Early Medieval Textiles and Costume and their Representations in Various Media

Whenever men and women are represented in the pictorial arts — especially whenever their official rank or function is emphasized — their clothes and accessories are an important part of the portrait. As comparatively few textiles and costumes are preserved from late antique and early medieval centuries, their reproductions in sculpture, paintings and other media may be considered as important documents, allowing us to visualize the richness of a material culture that would otherwise be lost. Not in all periods, however, do the pictorial documents mirror the decorative details of the reality, in which they were created, with the same degree of accuracy. Their testimony must, therefore, be checked against the evidence of surviving costume or textile fragments for a fair account of their credibility.

In a brief sketch — and more cannot be given here — it is not possible to give a detailed account of surviving documents and to follow closely the parallels and contrasts between textiles and their pictorial counterparts. Instead, several examples will be presented that demonstrate greater or lesser correspondence between textiles and their representations, indicating chances and risks of a method that might take the one as evidence for the other.

A recent study, published by Prof. Dr. Andreas Schmidt-Colinet¹, followed in detail the parallels between sculpture and textiles excavated in Palmyra and succeeded in proving that indeed the representations of costume and textiles have their foundation in the fabrics traded and used in the area.

The oasis of Palmyra was, from the 2nd century BC until the 3rd century AD, an important commercial centre trading silk and wool, spices, glass and ceramics between East and West. Remaining politically independent from Rome as well as from Iran, it entertained economically profitable relationships with both ruling powers and practically controlled the exchange of

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Fig. 1. Lid of a sarcophagus, found in temple tomb no. 176, Palmyra (photograph after A. Schmidt-Colinet, ed., Palmyra, Antike Welt 26/1995, fig. 50).

图 1. 棺盖，在巴尔米拉神庙发现，176号墓(取自 A. 施密特-科利内编：巴尔米拉，载《古典世界》 26/1995, 图 50)。
luxury goods between the Mediterranean and the eastern centres of Persia, India and China. Its inhabitants acquired considerable wealth that allowed them to wear costly costumes and to indulge in lavish decorations of their houses and tombs. In the latter, a number of portraits have been preserved that represent their patrons dressed in sumptuous garments decorated with elaborate patterns and finished with ornamental bands. Roman and oriental traditions, together with indications of rank and status, influenced the choice of dress; consequently the deceased might be clad in a Roman toga or in the Sasanian costume consisting of caftan and trousers respectively, in accordance with the image they wished to convey. Roman-style garments were decorated with clavi and ornamental borders, their patterns consisting of a variety of floriated tendrils or roundels filled with geometrically stylized flowers. The decoration of the oriental costume was more elaborate: Seams and hems seem to have been covered with braids showing intricate compositions of garlands and floral rosettes, or having geometrical motifs woven into the borders of the fabrics. Textiles used for mats and cushions were represented with a decorative grid system, the squares filled with star-shaped rosettes (fig. 1).

Silk and wool textiles found during excavations in Palmyra proved that these sculptures may indeed be considered as fairly exact representations of the actual textiles used: Woollen cloth with geometrical patterns in bold, contrasting colours (colour plate XIII, fig.1), tapestry-woven bands and roundels for the decoration of Roman-style tunics, intricate floral borders adorning the seams of the oriental caftans (colour plate XIII, fig. 2) and Chinese silks, probably used as decorative applications, were all identified in the necropolis of the oasis. Their evidence allows the study of the sculpture as documentary material for the actual costume and decorative detail. It should be mentioned, however, that colour schemes and textile qualities can be inferred only from the textile finds.

As a second example, textiles and their representations from Sasanian Persia are examined: Long after the art of silk weaving had been mastered in China, first efforts to follow its example were undertaken by its western neighbours in the 3rd and 4th centuries A.D., and by the 5th and 6th centuries there was quite an important silk production in what is now Iran, then the realm of the Parthians and their Sasanian successors. The Sasanians developed a very rich tradition in various arts and techniques (stone sculpture, metalwork and silk weaving featuring prominently among them) that were to have an enormous influence on their neighbours for centuries to come. And in these arts again we find remarkable parallels in the decorative elements, regardless of the material or technique used, and more to our point – an exact rendering of textile patterns and ornaments in the pictorial representations of costumes.

Aligned pearl roundels enclosing animals or fabulous creatures belong to the staple motifs of Sasanian art, decorating architecture, sculpture, metalwork and textiles alike. A particular composition, representing a simourgh (a fabulous beast made up of the head and body of a wolf, the claws of a lion, feathered wings and the tail of a peacock) is known from a stucco relief serving as an architectural decoration, a silver-gilt dish (fig. 2), a jug of the same material, and from the decoration of the caftan worn by a horseman in the famous relief of Taq-i-Bostan (fig. 3). The actual fabric of this garment has not been preserved, but there are a number of fragments surviving from silks woven in Sogdian in the 8th and the beginning of the 9th century closely following the Sasanian model (colour plate XIII, fig. 3). In other garments represented in the Taq-i-Bostan reliefs we can identify textile patterns featuring pheasants, peacocks and ducks, some in roundels, some without such an individual frame. All the motifs are known from existing Sasanian and Sogdian silk weavings. Here again, we may take the pictorial representations as reliable sources for a study of the contemporary textile decoration.

We must realize, however, that the evidence of the pictures is not always as reliable as the examples given above seem to suggest. A closer look at medieval documents revealed that sculpture, painting and book illumination sometimes at best just hint at the textiles and costumes worn and cannot be trusted as an exact description of material, decoration or usage.
After its impressive beginnings in China and Persia, the art of silk weaving moved farther west, reaching a new climax in Byzantium. From the 8th until the 11th century, we can follow the development of large-scale medallion patterns, heraldic animals of huge proportions in solemn procession, smaller motifs in geometrical arrangement and monochrome incised patterns with floral motifs set into ogival grids (colour plate XIII, fig. 4) respectively. In the contemporary representations of emperors and court officials, holy fathers or saints, we cannot identify any of these decorations. In costumes and furnishings, rendered with care in both wall painting and book illumination, fabrics are almost always given as unpatterned monochromes. If they do show a pattern, we cannot grasp more than an allusion to one of the compositions we know (fig. 8), and in the very rare cases where we recognize a known motif, the established dates for the actual textile and its representation are centuries apart. For Byzantium, it would not be possible to develop a thesaurus of textile patterns from the evidence of their representations in the pictorial arts.

Together with the documents from Palmyra and Sasanian Persia, this last example should be kept in mind as a warning: the pictorial sources may have a life and style of their own, and they may not have been meant to serve as a thesaurus of a reality lost ever since.

Notes

3 Schmidt-Colinet (ed.), Palmyra, op. cit., pp. 57-71 and the resp. figs.

Fig. 4. Menologion Basileios II, Rome, Biblioteca Apostolica Vaticana, Cod. gr. 1613.

图 4. 巴西尔二世的圣徒节日历，罗马，梵蒂冈使徒图书馆，Cod. gr. 1613。
古代晚期及中世纪早期的纺织品和服装以及它们在不同媒介中的表现

摘要

绘画艺术表现男女头部，尤其是要突出他们的地位和权势。这些人物所着的服装和装饰品就构成肖像的一个重要部分。由于中世纪早期的纺织品和服饰保存下来的寥寥无几，它们在雕刻、绘画和其它媒介中的再现便成为重要的资料，使我们得见或则就会失去的这一部分物质文化。当然，这些资料必须根据残存下来的服饰和纺织品来查证，以对其可信程度有正确的认识。

我们先来看看巴尔米拉的雕刻和纺织品。从公元前二世纪到公元三世纪，叙利亚的绿洲一直是东、西方之间经营丝绸、毛料、香料、玻璃器皿和陶瓷的贸易中心。其居民积攒下大量财富，其服饰华丽，房屋和陵墓装饰奢华。许多肖像雕刻得以在陵墓中保存下来，它们所表现的是死者的保护神。这些雕像衣着讲究，不仅装饰着复杂的图案，而且点缀着饰带。在巴尔米拉的考古发掘中发现的丝绸和羊毛织品表明，可能确实可以这样看这些雕像，即它们相当精确地表现了现实的纺织品，应当指出的是，它们的色彩只能通过纺织品文献来作出推测。

萨珊和早期波斯王朝的资料可拿来做对应的研究。萨珊王朝的统治者和军人的画像显示，他们的的衣着明显地具有地方特色。其式样和图案均有明确的规定。保存在教堂珍宝室的不全的纺织品和在考古发掘中发现的衣物(值得注意的是摩索乘瓦亚尔卡的考古发现，曾经于1967/7年在巴利利亚州国家博物馆展出)表明，这些肖像可以作为创建了这一地区重要传统的萨珊王室人员豪华服饰的参考资料。

无论何种我们所承认，画像作证据并不总象上面所引的、看来有提示作用的实例那么可靠。对中世纪的(更准确地说是拜占廷的)资料作一番仔细的审视表明，雕刻、绘画和古书插图中只多只暗示用过的纺织品和服饰，而不能看作是对材料和衣着习惯的准确描述。不管怎样，我们要想到这些实例，不把它们当作此后失去的现实的精确的类属词典。

(译者：陈钢林)
1: Cracks and flacks of polychromed terracotta, arisen in open room after excavation. – 2: Polychromed face of a terracotta in pit No. 3. The polychrome was painted with brush. – 3: Polychromed robe of a terracotta in pit No. 2. The terracotta was at first undercoated with putty, then with lacquer. – 4: A few samples with polychromy, after treatment with PEG and electron-beam.

1: 彩绘出土后，在敞开环境下，出现的破裂、翘起情况。 2: 三号坑一俑面部彩绘涂层。从照片上可以清晰地看出：彩绘是用毛刷刷涂的。 3: 二号坑一俑袍部的彩绘涂层。从照片可见：该俑在涂生漆底层之前，先用腻子在陶上进行打底处理。 4: 用 PEG 法和电子束法保护处理后的一些彩绘陶片。
1: 秦俑彩绘漆层干燥过程剧烈收缩, 从陶体上脱离。2: 漆(底)层失水收缩, 导致整个彩绘层(漆底层, 颜料层)脱落。3: 残片F-003/96经PEG200逐步处理, 两年以后的状态。4: 残片F-005a经PEG200逐步处理, 两年以后的状态。5: 残片F-002/96经保护处理, 两年以后的状态。6: 陶片F-006/96经保护处理, 两年以后的状态。7: 陶片F-008/96保护处理前。
1: The lacquer layer with polychromy of the terracota shrank drastically during the drying process and has peeled off from the terracotta.  
2: The lacquer undercoat shrank through loss of water, leading to the breaking off of the whole polychromed layers (lacquer undercoat and pigment layers).  
3: The phase of the sample F-003/96, two years after treatment with PEG200, step by step.  
4: The phase of the sample F-002/96, two years after treatment with PEG200, step by step.  
5: The phase of the sample F-006/96, two years after conservation treatment.  
6: The phase of the sample F-006/96, two years after conservation treatment.  
7: Sample F-008/96, before conservation treatment.  
8: Sample F-008/96, after conservation treatment.  
9: Sample F-007/98, four months after treatment.  
10: Sample F-003/98, four months after treatment, after optimised method.  
11: Sample F-012/98, four months after treatment, after optimised method.  
12: Sample F-013/98, four months after treatment, after optimised method.  
13: Polychromed samples of the terracotta army of Qin Shihuang, after treatment, soaked first with monomer, then consolidated with electronic-beam. The result was good.

1: Mural painting, Tang Dynasty; Mogao grotto, Dunhuang. – 2: Mural painting, Tang Dynasty; Mogao grotto, Dunhuang. – 3: Ming-Statue, Wofosi temple in Xiangshan, Beijing; azurite, with goldleaf, detail. – 4. a, b: Two Bodhisattvas, mural painting, Tang Dynasty; Mogao grotto, Dunhuang. – 5: Jiang Caiping, Old banana, traditional mineral pigment, 170 x 96 cm.

1: 敦煌莫高窟唐代壁画；2: 敦煌莫高窟唐代壁画；3: 北京香山卧佛寺明代塑像，石色，贴金箔，局部；4. a，b: 两菩萨，敦煌莫高窟唐代壁画；5: 老芭蕉，传统矿石颜料，170 x 96cm，蒋彩频
1: Bishamonten, Kaidan’in, detail of trousers; Tōdaiji, Nara, 9th century (Repro from: YOSHTAKA). – 2: Guanyin, 11th-13th centuries, front; Amsterdam, Rijksmuseum. – 3: Weituo Tian, Southern Song dynasty (1127-1278), detail of the sleeve with hemp-leaf decoration; Chōryūji temple, Gifu province (Repro from: YOSHTAKA). – 4: Guanyin, detail of leg and skirt; Amsterdam, Rijksmuseum. – 5: Tōji Kannon, 1232, detail of upper garment. (Repro from: YOSHTAKA)

1: 里沙門, 裤子局部; 东大寺, 奈良, 9世紀(取自: 义孝有贺); 2: 观音, 11-13世紀, 正面, 阿姆斯特丹皇家博物馆; 3: 韦驮天将, 南宋, 带大麻叶装饰的袖子局部; 岐阜县长沼寺 (Choryuji)(取自: 义孝有贺); 4: 观音, 大腿和裙子局部; 阿姆斯特丹皇家博物馆; 5: 东寺观音, 1232, 下衣局部(Choryuji)(取自: 义孝有贺)。
1: Inside of Henem's coffin: the yellow pattern is painted with pigments from the "jarosite minerals group" (Louvre AF 9757), © S. Joigneau, M. Louis.

2: Cross section of a woman's carnation sampled from the Akhetetep's mastaba (Louvre E 10958): 1-stone, 2-ground layer made of calcium sulphate, 3-yellow layer composed of pigments from the "jarosite minerals group", 4-copper chloride and calcium sulphate, © LRMF, S. Colmard.

3: Backscattered electron image of a part of the same cross section revealing the shapes and their heterogeneous size of the mineral grains, © LRMF, S. Colmard.

4: Pigments cakes stored in the Department of Egyptian Antiquities of the Louvre Museum. The turquoise colour belong to the Egyptian green. © LRMF, D. Vigiears.

1: 被看作大卫所画。卡特勒梅尔·德·坎西, 1779 年, 画布油画, 私人收藏。2: 3: 奥林匹斯的朱庇特的复原图 / 阿尔戈斯的赫拉的复原像, 卡特勒梅尔·德·坎西: 《奥林匹斯的朱庇特像》, 巴黎, 1815 年, 附页 / 图版 XX, 彩色版画, 慕尼黑巴伐利亚州国家图书馆, Res. Arch. 218m。4: 塞利农特的“恩培多克勒神庙的复原图”, 希托夫: 《塞利农特的恩培多克勒神庙的复原》, 巴黎, 1851 年, 图版 II, 慕尼黑巴伐利亚州国家图书馆, 2 Arch. 128°。
1: Greek terracotta figure, height 19.4 cm, c. 260 BC, Staatliche Antikensammlungen Munich (N 727). 2: Colour reconstruction of the West pediment of the Aphaia Temple (from: A. Furtwängler, Aegina. Das Heiligtum der Aphaia [1906], plate 104). 3: Archer from the West pediment of the Aphaia Temple (WXI), detail of the right hip and the right thigh, ultra-violet reflex shot. 4: Marble figure of an Archer (“Paris”) from the West pediment of the Aphaia Temple in Aegina (WXI), height 97 cm, c. 490 BC, Glyptothek Munich. 5: Detail of fig. 3: Archer (WXI). 6: Marble mould copy of the Archer from the West pediment of the Aphaia Temple (WXI), photo of the colour reconstruction (ochre tones not yet applied).

1: Tiger in black and red check, Warring States (475 BC-221 BC), embroidery with patterns of dragon, phoenix and tiger, excavated from grave No. 1 of Mashan in Jiangling, Hubei. — 2: Tiger in black and grey check, Warring States (475 BC-221 BC), embroidery with patterns of dragon, phoenix and tiger, excavated from grave No. 1 of Mashan in Jiangling, Hubei. — 3: With cinnamon dyed cloths, Western Zhou Dynasty (about 11th century BC-771 BC), excavated from graves of Earl Yu. — 4: A strip of silk with patterns of hunting, Warring States (475 BC-221 BC), excavated from grave No. 1 of Mashan in Jiangling, Hubei. — 5: Mirror cloth, tough silk, with stripes in black and yellow check (brocade), Warring States (475 BC-221 BC), excavated from grave No. 1 of Mashan in Jiangling, Hubei.

1: 江陵马山一号墓龙凤纹绣中、红相间的老虎; 2: 江陵马山一号墓龙凤纹绣中黑、灰相间的老虎; 3: 西周强伯墓群中染有朱砂的土块; 4: 江陵马山一号出土的田猎纹条; 5: 江陵马山一号墓出土的黑、黄相间的条纹覆鼻衣。
1: Embroidered silk quilt with pattern of coiling dragons and flying phoenix (detail), Warring States (475-221 BC); excavated in 1982 from grave No. 1 at Mashan in Jiangling, Hubei. – 2: Embroidered silk robe edge, with pattern of coiling phoenix and two dragons (detail), Warring States (475-221 BC); excavated in 1982 from grave No. 1 at Mashan in Jiangling, Hubei. – 3: Embroidered silk robe (so called Longevity Embroidery, detail), Western Han (206 BC-24 AD); excavated in 1972 from grave No. 1 at Mawangdui, near Changsha, Hunan. – 4: Embroidered silk robe (so called Riding Clouds Embroidery, detail), Western Han (206 BC-24 AD); excavated in 1972 from grave No. 1 at Mawangdui, near Changsha, Hunan. – 5: Silk gauze robe with printed and painted pattern (detail), Western Han (206 BC-24 AD); excavated in 1972 from grave No. 1 at Mawangdui, near Changsha, Hunan.

1: 江陵马山一号楚墓出土的蟠龙飞凤纹绣衾 (局部); 2: 江陵马山一号楚墓出土的二龙相蟠纹绣锦袍缘 (局部); 3: 长沙马王堆一号汉墓出土长寿绣锦袍 (局部); 4: 长沙马王堆一号汉墓出土云绣锦袍 (局部); 5: 长沙马王堆一号汉墓出土印花斿彩纱锦袍 (局部)。
1. Five directions (wufang: north, south, east, west and middle). Five Elements (wuxing: metal, wood, water, fire and earth) and five colours (wucai: blue, yellow, red, white and black).  
2. Brocade with inscription "chang bao zhi sun" (Preserve a flourishing growth of descendants), Han Dynasty, excavated in Loulan, Xinjiang.  
3. Brocade, Han Dynasty.  
4. Brocade with inscription "wu xing chu dong fang li zhong guo" (appearance of the Five Stars in the East is favourable to China), Wei and Jin Dynasty (220-420); excavated in Niya ruins, Minfeng county, Xinjiang.

1: 五方、五行及五色图示; 2: 新疆楼兰出土汉代《长葆子孙》铭文锦; 3: 汉代织锦; 4: 1995年新疆民丰尼雅遗址出土魏晋《五星出东方利中国》铭文锦。
1: Details of sculpture and woollen textile, found in tombs no. 186 and 46, Palmyra (photos after A. Schmidt-Colinet, ed., Palmyra, Antike Welt 26/1995, fig. 69 and 70).
2: Fragment of a tapestry-woven textile, found in the tomb of Kitont, Palmyra (photo after A. Schmidt-Colinet, ed., Palmyra, Antike Welt 26/1995, fig. 94).
3: Taq-i-Bostan relief representing a horsemman, detail of garment (photo after K. Erdmann, Die Kunst Irans zur Zeit der Sasaniden, Mainz 1969, fig. 97).
4: Caftan found in Moalleva Balka, weft-faced compound twill with simourgh pattern, detail; St. Petersburg, State Hermitage, inv.-no. Kz 6584. Chasuble of the archbishop Willigis (reg. 975-1011), monochome weft-faced compound twill, detail; Munich, Bayerisches Nationalmuseum, inv.-no. T 11/170.

1: Lacquer box in the shape of a mandarin duck with scenes of dance and music. Warring States. Excavated from the grave of Marquis Yi of the Feudal State of Zeng in the district town of Suizhou, Province of Hubei. – 2: Bowl with two handles in the shape of a butterfly, painted. Warring States. Excavated from grave No. 2 in Wangshan near the district town of Jiangling, Province of Hubei. – 3: Decoration on the black ground of a lacquer coffin, detail. Han. Excavated from grave No. 1 in Mawangdui near Changsha, Province of Hunan. – 4: Lacquer ware with gold leaf or gold powder. Qing Dynasty.

1. 彩绘蒲葵碟；彩绘乐舞图，战国，湖北随州曾侯乙墓出土；
2. 彩绘蝶形漆耳杯，战国，湖北江陵望山2号墓出土；
3. 彩绘黑地漆棺漆画（局部），汉，湖南长沙马王堆1号墓出土；
4. 彩绘漆器，清
1: Amulet (for description see text).  2: Octagonal Freer Gallery stick (diameter 8.5 mm).  3: Microscopic picture of single crystals of Chinese Blue, Ba-CuSi_2O_6.  4: Microscopic photograph of the pigment layer of sample I of the Terracotta Army. These pigments are Chinese Purple and Cinnabar. Reprint with permission from Thieme, 1995.  5: From left to right: Barium-Copper-Oxalate, BaCu(C_2O_4); product of the reaction of Chinese Purple with oxalic acid; mixture of Chinese Blue and Purple; Chinese Purple.  6: Photograph of the cylindrical seal (for description see text).  7, 8: Growth of lichens. The central ring was mixed with Egyptian Blue (above) and Chinese Blue (below). No growth is seen in the central areas confirming the fungicidal effect of these pigments.

1: Amulett. 照片 (说明见报告);  2: 弗里尔画廊样品的八角形平板 (直径为 8.5 mm);  3: 中国蓝的单晶体的显微镜照片, BaCuSi_2O_6;  4: 兵马俑一例颜料层的显微镜照片, 颜料为中国紫和朱砂。重印经蒂美许可, 1995;  5: 从左至右: 草酸钡铜, BaCu(C_2O_4); 中国紫与草酸反应的产物; 中国蓝和紫的混合物; 中国紫;  6: 圆柱形图案照片 (说明见报告);  7, 8: 地衣的生长, 中心与埃及蓝 (上图) 和中国蓝 (下图) 混合。中心区未见生长, 证实这些颜料所具有的杀菌功能。
1: Buddhist statues, polychromed clay, Tang Dynasty, Dunhuang, cave 460. The figure on the left was damaged, it shows its wood brace and splendid chnatherum. – 2: Buddha, polychromed clay, Northern Wei (386-534), Dunhuang, cave 254. The upper limbs are broken. You can see the inner stone body. – 3: Bodhisattva, polychromed clay, Dunhuang, cave 45 (Tang Dynasty). Rich polychromy and gilded parts on the dress. – 4: Buddha, polychromed clay, Northern Liang (397-439), Dunhuang, cave 275. Thrifty and simple polychrome. – 5: Bodhisattva, polychromed clay, Tang Dynasty, Dunhuang. On the altar in cave 205. The minium is changed. – 6: Buddhist statues, polychromed clay, Dunhuang, cave 335. The figures were painted in Qing Dynasty.

1: 黃窩第460窟唐代彩塑，左側脅像已損壞，露出木骨架和及及皮草；
2: 黃窩第254窟北魏彩繪佛像，上肢斷裂，露出石胎岩體；
3: 黃窩第45窟唐代洞窟中彩繪富麗并裝飾上裝金的菩薩像；
4: 黃窩第275窟北涼洞窟中，彩繪簡朴的佛像；
5: 黃窩第205窟佛堂上，鉛丹已變色的唐代菩薩塑像；
6: 黃窩第335窟中，被清代重塑和重彩的彩塑。
1: Painted decoration, Gate of Martial Spirit (Shenwumen), Forbidden City, Beijing.  
2: Painted decoration with dragon and phoenix pattern at ceiling, Palace of Longevity and Good Health (Shoukanggong), Forbidden City, Beijing.  
3: Painted decoration, two dragons playing with a pearl, Hall of Pleasantable Old Age (Leishougong), Forbidden City, Beijing.  
4: Painted decoration, Meridian Gate (Wumen), Forbidden City, Beijing.  
5: Caisson ceiling with golden dragon, Hall of Imperial Supremacy (Huangdiyuan), Forbidden City, Beijing.  
6: Painted ceiling with round cranes, Palace of Great Happiness (Jingfugong), Forbidden City, Beijing.  
7: Painted ceiling with frontal dragons, Hall of Preserving Harmony (Baochedi), Forbidden City, Beijing.

1: 神武门彩画; 2: 寿康宫龙凤天花; 3: 乐寿堂双龙戏珠彩画; 4: 午门彩画; 5: 皇极殿藻井; 6: 景福宫团鹤天花; 7: 保和殿正面上龙天花。
△ 8. Painted ceiling, mantra with six characters, Buddha niche, Hall of Comprehensive Correspondence (Xianruoguan), Forbidden City, Beijing. 

△ 9. Painted decoration with haiman pattern (cloud, flowers and plants), Study of Jiangxue (Jiangxuexun), Forbidden City, Beijing. 

△ 10. Painted ceiling with haiman pattern (Chinese wisteria), Study of Tiredness with Diligence (Juanqinzhai), Forbidden City, Beijing. 

△ 11. Painted decoration, Hall of Mental Cultivation (Yangxindian), Forbidden City, Beijing. 


△ 13. Painted decoration, Study of rinsing of fragrant (Shufangzhai), Forbidden City, Beijing. 

△ 14. Painted decoration, Study of rinsing of fragrant (Shufangzhai), Forbidden City, Beijing.

15: Vase, painted pottery, Neolithic Age.
16: Guardian Warrior, painted earthenware, covered with gold leaf, Sui Dynasty.
17: Court Maid, painted clay, Qing Dynasty.
18: Avalokitesvara, wood, Ming Dynasty.
19: Arhat, painted clay, Ming Dynasty.
20: Buddha, painted clay, Tibet, Qing Dynasty.

中国漆艺髹饰技法

漆艺，漆工艺，漆艺术之意。包含了实用的漆器，欣赏的漆画和漆塑，它是一门综合性的艺术。

漆艺之“漆”，又称大漆，生漆，土漆，天然漆。……足是用过过滤，搅拌，晾晒等精制过程，方可应用。

漆艺之“髹”，又称大漆，生漆，土漆，天然漆。……足是用过过滤，搅拌，晾晒等精制过程，方可应用。

具有抗潮防腐，耐酸耐碱，耐热绝缘等性能，又有美丽柔和的光泽，因此它是很好的涂饰材料，素有“漆料之王”的美誉，广泛地应用于工业，建筑和艺术。

我们的先人在数千年中和漆打交道的过程中，创造了多种多样的髹饰技法。所谓“髹”，即用刷，刷，贴，木炭等手段涂饰在木器，漆器上进行装饰，分述如下。

一：髹饰。以漆(包括调制颜料的彩漆)直接涂饰的方法。是最基本的方法。以黑，红色为最多。黑即漆之本色(漆木为棕色，稍厚即近黑色)。中国有“漆黑”的词汇，红色即天然硫化汞-朱砂(红)漆。即鲜艳，又稳定，历久不衰。中国古有“丹漆不文，白玉不雕”之说，以示对朱漆的赞美。自古至今，黑和红成为漆艺的主要色彩。以黑漆漆饰者为“黑髹”，以朱漆漆饰者为“朱髹”。此外还有“金漆”(通体贴金)、“彩漆”……。

二：描绘。以漆或金银描绘饰物的方法。可以分描绘，彩绘，晕金等不同类型。

1. 彩绘：最常见的就是单色彩绘，如楚汉时的漆器，多是在黑漆底上画黑纹，或者在朱漆底上画黑纹。也多色并施者。

2. 彩绘：利用漆的粘性，在漆液干干不干之际粘贴金箔或金银粉的方法。

3. 晕金：在将干未干的漆面上敷粘金银粉，以金银粉之疏密来表达形式变化方法。

以上三种方法可以相互结合起来运用。

三：镶嵌。利用漆的粘性，把自然界中的美材，如金银，贝壳，玉石等镶嵌于漆物上的方法。

1. 嵌金银：将金箔片或银箔片刻成纹样粘于漆面，再涂漆磨显。唐代称此为金平脱或银平脱。日本称为“平脱”。现代称为镶嵌银者。

2. 嵌螺钿，把贝壳加工成薄片粘贴于漆面，再涂漆磨显。有软螺钿和硬螺钿之别，前者螺钿片薄，又称薄螺钿，后者螺钿片厚，又称厚螺钿。

3. 嵌蛋壳。这是现代的镶嵌方法，蛋壳镶嵌不仅解决了漆艺的白色，同时又有美丽的龟脊肌理。不仅可以镶嵌成白文，还可以镶嵌成白地；不仅可以镶嵌，还可以嵌金。

四：刻顶。在漆底上用刀，针刻处纹样，可以刻点，也可以刻线。然后细金，银或彩。有雕金，雕银，刻漆三种类型。

1. 钩金，又称为“细推”、“针刻”，多为刻细，也可以刻点，点分疏密。刻后填金者称“钩金”；填银者称“钩银”；填彩者称“钩彩”。

2. 勾雕：和钩金法基本相同。不同在于刻后填彩漆，干后研磨，致彩齐平。细多用此法。

3. 刻漆：又称“刻灰”，漆层较厚，多刻块而留阳纹，内填彩色，不必求平。古称“刻彩”，多用来制作屏风大件作品，有版画风采。

五：磨绘，漆液干后很硬，耐用石头，木炭，木炭纸等研磨。磨绘即是在层层描绘涂漆之后再磨出纹样效果的方法。有以下几种类型。

1. 彩绘磨绘：先用彩漆描绘纹样，再通体涂漆，干后磨显。

2. 罩描磨绘：利用漆的半透明特性，罩磨塞金或彩漆，再磨出磨显效果。

3. 间绘：用金，银箔或粒状物或干漆粉等覆盖纹样需要磨成厚密之漆，再磨出磨显。日本称此道。

4. 铜箔磨绘：这是当代的磨饰方法，即在铜箔上罩涂透明松再研磨出明暗层次的方法，透明性漆中加入透明颜料，常用来表现人物的肌肤。

六：变涂。用某种工具(如刷锋，滚珠)，或某中介物(如纸片，树叶，粒物)……，或用汽油，樟脑油等漆稀释……以引起抽象纹理的方法，千变万化，古称“彩繪”，日本称为“变涂”。

七：堆塑，用调漆打拓，或漆中拌进填充料(如硫粉，珍珠等)原地纹样如浮雕的方法。

八：雕漆。涂漆数十道，上百道，数百道……待到所需的厚度，再用刀雕刻的方法。根据漆的色彩不同，用刻红，刻黑，刻白，刻彩别。

1. 刻红：纯以朱漆雕刻者。

2. 刻黑：纯以黑漆雕刻者。

3. 刻白：以黑，朱色漆相间者。

4. 刻彩：多色者。

中国古代，如战国，秦，汉时期的漆器多用髹饰雕刻技法，唐代出现了金银镶嵌，宋元又发展了雕漆，至明清技法就更加多种多样了，中国当代的漆画，各种髹饰技法得到更综合的运用。

多种多样的漆艺髹饰技法，开拓了丰富多彩的漆艺之美，创造了光璀璨的漆艺文化。中华漆艺不仅是一门历史悠久的传统艺术，同时也是一门富有广泛开发前景的现代艺术。
Qi-Shiguang

Qi-Lacquer — Technique and Art

The lacquering, the art of lacquer means the technology of applying lacquer. It is a traditional Chinese art.

The lacquer also called big lacquer, raw lacquer and rhus lacquer, is a natural paint derived from the varnish tree. It is not only water-proof and antiseptic but also lustrous. In China, it began to be used six or seven thousand years ago to protect and beautify articles and utensils, for example the wood raw lacquer bowl unearthed from the 3rd level of Mudu Culture in Yuyaohe of Zhejiang Province. The black lacquer mug and the black lacquer jar, both made of pottery and unearthed in Wujiang of Jiangsu Province, are relics from the Liangzhu Culture about 4 or 5 thousand years ago.

The liquid lacquer may be applied not only to wood and pottery but to metal, leather and bamboo as well. In addition, it can be combined with linen to form multi-layered patterns by taking advantage of the lacquer’s adhesiveness and the linen’s tensile force. Using this method, which was called “Jia” in ancient times and is used on lacquer sculpture works, any pattern you wish to have, can be formed.

The lacquering work falls into many varieties and the coating methods are also diversified including coating and painting, inlaying, carving and filling, polishing and painting, embossed sculpture, carved lacquering, etc.

1. Coating and painting refers to the method in which lacquer is blended with pigments, gold or silver to then be applied by brush as a coating or as designs and pictures.
2. Inlaying refers to the method of inlaying shells, jade or metal onto the surfaces by using the adhesiveness of the lacquer.
3. Carving and filling refers to the methods by which decorative patterns are first carved by a needle or a knife on the surfaces and then filled in with gold, silver or colour lacquer.
4. Polishing and painting refers to the method of first applying colour lacquer (including gold and silver) layer by layer, then polishing the surface and grinding patterns with water-proof abrasive paper or grinding stones.
5. Embossed sculpture refers to the method of using lacquer or the mixture of lacquer and fillings to project the patterns.
6. Carved lacquering refers to the method of carving which is done after dozens or even hundreds of lacquer coatings are completed.

The diversified coating and lacquering methods produce both lacquer wares of practical use and artistic works of painting and sculpture. It is a comprehensive art form, which uses various materials and combines practical art with pure art. It is not only traditional but also promising in its developing prospects. See colour plate XIV.
Chemical and Physical Investigations of Egyptian and Chinese Blue and Purple

Hans-Georg Wiedemann* and Heinz Berke**

* Mettler-Toledo GmbH, CH-8603 Schwerzenbach
** Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

Introduction

The production of Egyptian Blue can be traced back from earlier than 3000 B. C. up until approximately 300 A. D. One of the earliest documentation of Egyptian Blue is found on the Tablets of an olive oil container, which certifies the quality of the oil blessed by the Goddess Iset (pre-dynastic). Another proof for the early use of Egyptian Blue is the Mastaba of the vesir of Mere-ruka (2300 B. C., Saqqara). This and other samples are shown in Table 1 and represent a selection of identified Egyptian Blue up to the Greek-Roman period.

A contemporary artist, E. Arpagaus, has studied mineral colours and pigments of Egypt and surrounding areas (Arpagaus, 1996) showing the variety of different colours, which were prevalent in nature. The presented blue pigment has however been artificially produced in the manner of the Egyptians.

In ancient times continents and countries were connected by famous trade routes; the link between the Western World and ancient China was established via the Silk Road. Aside from its economic function this adventurous and risky route played an outstanding role in the distribution and exchange of ideas and technologies between East and West. The relatively constant composition of Egyptian Blue over the period of the Old Kingdom up to the Ptolemaic and Greek-Roman time (Table 2) indicates that the information about the production of coloured pigments never got lost. For blue pigments this is attributed to the fact that they had a prominent role in religious rites and everyday life. States adjoining the Silk Road were challenged by the tradition of blue production and its use in manufactured Egyptian goods to either obtain it by trade or to produce it themselves. This background was apparently a major driving force for the expansion of artificial blue and even other pigments.

The change in location and the need for further improvements of artificial pigments induced new technological developments, which generated similar advanced materials such as strontium and barium copper silicates as in the Iraqi and Iranian samples of Brick Nimrud (British Museum London) the Sistram Hasanal and the Goblet Hasanal, Iran (both Metropolitan Museum New York) and barium in Chinese artefacts represented by the blue and purple octahedral sticks and samples of the Terracotta Army, all compiled in Table 1.

The Chinese samples are attributed to the Warring States, Qin and Han period 600 B. C. till approximately 200 A. D. As we will see in the later context they contain man-made blue and purple pigments called Chinese Blue and Purple, sometimes also denoted as Han Blue and Purple (Fitzhugh, 1992). They were used in colouring applications and they refer to destinct, but very related chemical compounds. Only Egyptian and Chinese Blue are found as minerals in nature (Cuprorivaite, Effenbergerite (Giester, 1994)). They are, however, so rare that any utilization of these minerals by ancient civilizations can be excluded. It should be mentioned at this point that the only mineral pigment used by earlier civilizations, which naturally appeared blue and did not demand chemical transformation or processing, was lapis lazuli (Reine, 1999). Its scarcity in nature caused it to become highly esteemed, at least in the western hemisphere. Presumably as a consequence of the general scarceness, the blue has been attributed divine character in some civilizations, such as the Egyptian.

In general colour has played a major role in the development of civilizations and has acquired important cultural functions as one of the essential ways of human self-expression and affectation. Colours produce aesthetic stimulation, which is reflected in art forms. All this emphasizes the outstanding role of colour in human development, and colouring substances in the form of pigments have thus always been used by mankind as they became available.

Apparently motivated by the lack of natural blue minerals and mankind's intrinsic desire for colours, people were driven to invent blue pigments. It is may be worth mentioning that among those invented Blues there is also the Indigo based Maya Blue, which had wide-spread application within Indian cultures (José- Yacaman, 1996). Any of the mentioned man-made blue pigments but also Chinese Purple required sophisticated chemical and technological developments, which could only be mastered in a sound cultural and technological environment. In the following article we will see that the chemistry behind these man-made pigments is quite complicated. Ancient chemical achievements could not be based on atomic or molecular grounds. Therefore any progress was established by long and tedious processes of empirical probing.

Investigated Original Samples of Egyptian Blue, Chinese Blue and Purple

The investigated ancient samples of Egyptian Blue and Chinese Blue and Purple are summarized in Table 1. The Egyptian samples cover a span of almost 3000 years starting with Blue from the 6th Dynasty of the Old Kingdom to the Roman time.

The oldest sample stems from the Mastaba of Mere-ruka in Saqqara, Egypt. Mere-ruka was vesir to King Teti, reaching the Mastaba from his tomb through a fictive door to receive the daily sacrifice from his relatives, who prepared the altar (Wiedermann, 1997b). The second sample originates from the tomb of General Antef, Middle Kingdom, 11th Dynasty. General Intef reported to Mentuhetep II as the commander of the troops. He belonged to the most important courtiers, which is also expressed by the location of his tomb in close vicinity to the funerary temple of his King in Thebes. The next three samples studied came from the New Kingdom period. Blue from the crown of the famous bust of Nefertite (Ägyptisches Museum der Staatlichen Museen Berlin, Germany) and Blue of the Talatat Stones of the Temple of her husband Echnaton (Amarna, Egypt). The cylindrical seal, which is also dated to the New Kingdom and whose origin falls into a very productive period for artisans,
is the property of one of the authors (fig. 1). It has been described in detail elsewhere (Wiedemann, 1997a). The sample of Brick Nimrud comes from Mesopotamia and is dated to the 13th – 7th century B.C. Today it is the property of the British Museum, London.

The Late Egyptian Period is documented by several other samples. Amulet Bes was protecting those who wore it by the powers of the dwarffish God Bes. It is dated to the 24th Dynasty and is the property of one of the authors (colour plate XV, fig. 1). The wooden falcon figure Ba-bird (Kestner Museum, Hannover, Germany) contains blue areas, from which a sample was studied. Ba-bird from approximately 500 B.C. symbolized a protection god at burial ceremonies (Wiedemann, 1997b). The figure Ptah-Sokaris-Osiris from the 1st century B.C. stems originally from Memphis, Egypt. It is now property of the Staatliche Sammlung Ägyptischer Kunst, Munich, Germany (ÄS 19). It served as a container for corpses. A sample of the Blue was taken (Wiedemann, 1997b). The samples of the mummy cartonage and the mummy coffin represent Egyptian Blue from Ptolemaic and Roman times. Their present locations are unknown.

Four of the six originally investigated samples of Chinese Blue and Purple (Table 1) were taken from original Blue or Purple sticks of octagonal shapes. It is thought that these sticks were trade items. They were used as pigment bases in paints and applied by grinding. The general phenomenology of the Freer Gallery sample has been described earlier by FitzHugh (FitzHugh, 1983; FitzHugh, 1992). The photograph of a slice of the Freer Gallery sample (colour plate XV, fig. 2) shows its purplish blue colour and the representative size of such sticks.

The Royal Ontario Museum Sample stick came from a blue octagonal stick said to have come from Jinen near Luoyang, China (FitzHugh, 1992). It is reported to be made of mainly blue particles with scattered purple ones. The two samples of sticks from the Museum of Far Eastern Antiquities in Stockholm, K 4069 (Blue) and K 4070 (Purple) are described as worn and porous materials (FitzHugh, 1992), from which powdery material was taken for investigation. The stick samples were recently discussed (Berke, 2000).

Distinct samples from different parts of the Terracotta Army (sample I and II), were investigated as cross sections of the pigment layer. Earlier investigation showed the presence of Chinese Purple and other pigment materials (Herm, 1995; Thieme, 1995). Application of Raman spectroscopy and electron microscopy with EDX were expected to confirm these results, but also to deliver further information on the nature of the pigment content. Colour plate XV, fig. 3 shows the microscopic photograph of one of the studied cross sections (sample I) containing a crystalline of Chinese Purple.

All the samples were compared to pure Egyptian Blue and Chinese Blue and Purple or their mixtures, obtained by contemporary independent synthesis (among others Bayer, 1991).
Chemistry of Egyptian and Chinese Blue and Chinese Purple

Compositions and Structures

Egyptian and Chinese Blue are calcium and barium copper silicates with the compositions CaCuSi₄O₁₀ and BaCuSi₄O₁₀, (Finger, 1989; Fitzhugh, 1983; Fitzhugh, 1992) respectively. They thus differ in the replacement of calcium with barium. Their chemical relationship is so close that crystals of both compounds adopt exactly the same habitus (Pabst, 1959; Chase, 1971; Bayer, 1976) and on the microscopic scale they are isomorphous. Their structures consist of puckered infinite silicate layers composed of (SiO₄)₄, silicate squares, which are condensed together via oxygen bridges and thus form a two-dimensional network of connected (SiO₄)₄ and (SiO₃)₃ rings. Each silicon atom bears a terminal oxygen group, which can either contribute to binding of Cu²⁺ or Ca²⁺/Ba²⁺. As sketched in fig. 4 four oxygen atoms from a silicon atom of four adjacent (SiO₄)₄ rings accommodate a copper ion in square planar arrangement. The calcium or barium ions are employed in a similar fashion, however in an alternating way, with the copper they twice pick four oxygens from two adjacent layers for binding and in this manner, they 'glue' the layers together.

![Schematic representation of the puckering of a Si₄O₁₀⁻ layer in Ca, BaCuSi₄O₁₀ induced by Cu²⁺ coordination. Every other open square is filled by Cu²⁺. The non-filled squares are occupied by Ca²⁺ or Ba²⁺ connecting the layers. The structure of Egyptian Blue was determined by Pabst (Pabst, 1959) and redetermined by Bensch (Bensch, 1995). The structure of Chinese Blue was studied by Finger (Finger, 1989).](image)

Fig. 1. Schematic representation of the puckering of a Si₄O₁₀⁻ layer in Ca, BaCuSi₄O₁₀ induced by Cu²⁺ coordination. Every other open square is filled by Cu²⁺. The non-filled squares are occupied by Ca²⁺ or Ba²⁺ connecting the layers. The structure of Egyptian Blue was determined by Pabst (Pabst, 1959) and redetermined by Bensch (Bensch, 1995). The structure of Chinese Blue was studied by Finger (Finger, 1989).

In CaCuSi₄O₁₀ and BaCuSi₄O₁₀ the copper ions are thus in a very similar oxygen atom environment. Since the pigment properties, e.g. the blue colour, are merely related to the copper ions (chromophore), both compounds have almost the same colour properties. The structure of Egyptian Blue was first unravelled quite some time ago (Pabst, 1959; Bensch, 1995), while that of Chinese Blue has been elucidated more recently (Finger, 1989). It is a frequent observation, that layered structural frameworks with preferred spatial orientations of the chromophores give rise to pleo- or dichroism. Two or more different colours (dichroism or pleochroism) can be seen in different orientations of the crystal faces when irradiated with (white) light. Egyptian Blue does show pleochroism (Bayer, 1976) and due to the close structural resemblance of Egyptian and Chinese Blue, we can assume that Chinese Blue is also pleochroic. When grinding is applied to solid matter, particle size, crystal shape and crystal face distributions are changed and subsequently the overall colour appearance may concomitantly be altered. While large platelets of Egyptian or Chinese Blue appear light blue (colour plate XV, fig. 3), when grinding is applied, both pigments becomes more bluish. This is illustrated in photographs of powders of the Chinese pigments (colour plate XV, fig. 5).

Chinese Purple's composition is BaCuSi₄O₁₀. It formally contains two equivalents of quartz (SiO₂) less than Chinese Blue. It should be mentioned at this point that an analogous 'Egyptian Purple' with the formula CaCuSi₄O₁₀ could to date not be prepared. Chinese Purple may be viewed as a reaction intermediate (so-called kinetic product) while producing Chinese Blue. Even though Chinese Purple also consists of layers in its microscopic structure (fig. 7a and 7b), these layers differ significantly in their basic structural motifs from that of Egyptian and Chinese Blue.

There is no other extended silicate framework like that of the Blues. The silicate condensation process is stopped at the (SiO₄)₄ ring stage generating a patchwork of isolated Si₄O₁₀⁻ fourring units infinitely connected by Cu-Cu bonded moieties to build-up a Cu₂Si₄O₁₀⁻ layered structure (Janczak, 1992). Like in Chinese Blue the barium ions are located between the layers and hold these together by coordinative contacts. Figure 7b also shows a piece of a [Cu₃Si₄O₁₀⁻]⁻ layer as taken from a single-crystal X-ray structure of Chinese purple.

The extraordinary and very unique feature of this structure is tighed up to the copper-copper bond, which was overlooked in the earliest structural determination of Finger et al (Finger, 1989). This inner core of the structure of Chinese Purple is thus related to the dimer of prototypical copper acetate, Cu₃(acetate)₆, which also contains a bridged Cu-Cu unit, where the bridging functions are provided by the acetate ions. Early Chi-

![Schematic representation of the structure of Chinese Purple with the principle arrangement in layers of Ba²⁺ and Cu₂Si₄O₁₀⁻.](image)

Fig. 2a. Schematic representation of the structure of Chinese Purple with the principle arrangement in layers of Ba²⁺ and Cu₂Si₄O₁₀⁻.
Chinese chemists were thus, to our knowledge, the first humans to prepared a chemical compound containing a metal-metal bond. This peculiar finding is even more important in view of the chemical fact, that in compounds other than in metals, metal-metal bonds still have nowadays the flair of curiosities.

It is important to note that in Chinese Blue and Purple the copper ions are rigidly fixed in the structural framework. As a consequence of that, they can effectively absorb and emit light: the latter is effective, when excited by light with short wavelengths inducing fluorescence (Ajo, 2000). Layered structures such as Chinese Purple are also expected to display pleochroic features similar to those of Egyptian and Chinese Blue. On grinding, Chinese Purple changes its colour tone from more bluish to more purplish (colour plate XV, fig. 5).

Stability Properties of Egyptian and Chinese Blue and Chinese Purple

The thermal and chemical stabilities of Egyptian and Chinese Blue on the one hand and Chinese Purple on the other are strikingly different. This can be related to two structural factors:

(a) contrary to Egyptian and Chinese Blue the silicate framework of Chinese Purple consists of relatively small SiO$_4^{4-}$ units connected by only weak coordinative bonds to copper and barium

(b) Chinese Purple contains a chemically labile Cu--Cu bond

The more silica-rich Egyptian and Chinese Blue are more SiO$_4^{4-}$-like with a higher degree of condensation in the silicate framework. Melting, which requires breakdown of the silicate layers into smaller molecular units, is thus only possible at elevated temperatures. This was confirmed by an isothermal heat treatment of corresponding Chinese samples at 1200 °C for four hours. Pure Chinese Purple melted to a viscous, black green glass, whereas Chinese Blue only showed increased sintering. X-ray investigation of these samples quenched from 1200 °C proved that the former was amorphous and vitreous, while the latter was unchanged BaCuSi$_2$O$_8$. BaCuSi$_2$O$_8$ actually starts to decompose at 1170 °C under loss of O$_2$. It can however be reoxidized completely at 1060 °C. (Wiedemann, 1997b; Bayer 1976). The thermal decomposition of Chinese Purple is expected to take place according to the following equation

$$3 \text{BaCuSi}_2\text{O}_8 \rightarrow \text{BaCuSi}_2\text{O}_{10} + 2 \text{BaSiO}_3 + 2 \text{CuO}$$

Barium and copper meta-silicates are formed first, the former has even been detected in experiments under melt conditions (Bayer, 1991). At temperatures above approximately 1000 °C the potential decomposition product Cu$_2$SiO$_4$ (dehydrated diopside) is known not to be stable and to liberate tenorite and quartz (Kiseleva, 1993), the latter may subsequently be consumed by Chinese Purple to generate Chinese Blue. Under conditions of above 1050 °C the copper(II) oxide content of these compounds could furthermore turn into copper(I) oxide and oxygen:

$$2 \text{CuO} \rightarrow \text{Cu}_2\text{O} + 1/2 \text{O}_2$$

Prolonged firing of Chinese Purple thus results in additional formation of Chinese Blue, colourless barium meta-silicate and red cuprite (Cu$_2$O). Powdered mixtures of these constituents would actually generate a more reddish appearance of the Chinese Purple, the more the higher the cuprite content is. All of these components have been identified in samples of Chinese Purple made by independent synthesis, and which underwent prolonged thermal treatment.

What both, the Egyptians and the Chinese could not know, was the reactivity of their pigments in the presence in chemical or biological agents. In acids a striking difference in the chemical stability of Chinese Purple and Chinese Blue was observed (Pabst 1959; FitzHugh 1983) and could be confirmed by our
own experiments. Egyptian and Chinese Blue are stable in dilute acids, whereas Chinese purple, BaCuSi$_2$O$_6$, rapidly fades and decomposes. The same effect is observed when these pigments are exposed to an aqueous solution of oxalic acid. As products Ba- and Ca-oxalates could be identified by EDX, X-ray diffraction and simultaneous thermogravimetry / mass spectrometry investigations (Lamprecht, 1997). This is an important finding with respect to conservation procedures, since it demonstrates that in the deterioration of works of art, lichens, which excrete oxalates or even oxalic acid, may play a relevant role (Seaward, 1989).

In turn, it has been shown in previous investigations on coloured Egyptian papyri, that spores and fungi did not exist in areas where Egyptian Blue was used as a pigment. These findings were confirmed by further studies of different papyri. This can be explained by the fact that copper is a strong fungicide, which was proven by experiments with limestone covered by lichens. No further growth occurred in areas where the lichens were removed and which was subsequently painted with Egyptian Blue (Wiedemann, 1996; Lamprecht, 1997) (colour plate XV, fig. 7, 8).

It is interesting to note that the production of blue bread is mentioned in documents of the 18th dynasty (1500 B.C.) in ancient Egypt (Sethe, 1961). Since the Egyptians produced air-dried bread for emergency situations, it may be that they had some knowledge about the conservation effect of Egyptian Blue. As shown in figure 8 Chinese Blue has similar fungicidal properties. Chinese Purple, however, deteriorates under the influence of oxalate producing lichens and leaves light blue residues behind. Chemical reactions of Chinese Purple with oxalic acid produced a double salt BaCu(C$_2$O$_4$)$_2$ of light blue colour (colour plate XV, fig. 7, 8). It is therefore probable that the light blue colour of the trousers of some Terracotta Warriors (Leederose, 1992) may not be the original colour, but rather the transformed Chinese Purple, which occurred under the influence of oxalate excreting lichens.

**Synthesis of Egyptian Blue**

Preparation of Egyptian Blue has been carried out by our group and others. In our search for optimal conditions for the preparation, various techniques have been reported. The synthesis of Egyptian Blue was mostly in powdery form as a pigment, but also as a compact body. The effect of the firing temperature and of the atmosphere on its formation and stability has been demonstrated elsewhere (Bayer, 1976). The effect of various fluxes on the development of the tone of blue colour has been confirmed by microscopical light studies. Compact bodies were produced either directly from mixtures of the raw material or from presynthesized Egyptian Blue by heating the dry-pressed powders at 900 °C in air. This proved that, in the raw material samples, the flux (Na$_2$CO$_3$) migrates and is concentrated in the surface, whereas the flux-free interior remains greenish and practically does not react. On the other hand the compact bodies made from presynthesized Egyptian Blue powder are less intensively coloured, but blue throughout. The morphology of the surface of the compact bodies reveal CaCuSi$_2$O$_6$ crystals embedded in the flux materials. Single crystals of Egyptian blue could be prepared by long-time annealing (100 h, 880 °C) of a borax-flux containing mixtures of the raw materials. Based on the results of synthetic experiments, it seems probable that the fine-textured Egyptian blue objects, e.g. cylinder seals, were made by a two-stage firing cycle in oxidizing atmosphere. A single firing at 900 °C of bodies formed directly from the raw material mixture leads to fragile structures. This is due to the migration of alkali flux to the surface, forming a coarser-textured surface layer of Egyptian Blue, but leaving the bulk unreacted and greenish coloured. Therefore, the preferred method would be first to synthesize the Egyptian blue pigment, then the finely ground material can be used for forming the objects with addition of an organic binder (e.g. gelatine or wax) in order to get sufficient strength. For improved sintering at 900 – 950 °C it is of advantage to add some flux or even better to add glass powder. These additions form a grain boundary melt, which enhances the liquid phase sintering. The objects should not be heated higher than 1000 °C, since above this temperature Egyptian Blue decomposes irreversibly to tridymite and glass.

**Synthesis of Chinese Blue and Purple**

Detailed studies on the chemical composition, as well as of the phase diagram of this Ba-Cu silicate-system revealed that there exist – in contrary to the mentioned Egyptian Blue, CaCuSi$_2$O$_6$ – at least four stoichiometric ternary phases (Finger, 1989; Malinovskij, 1984; Tsukada, 1999):

BaCuSi$_2$O$_6$ (blue), BaCuSi$_2$O$_6$ (purple), BaCu$_2$Si$_3$O$_9$ (blue), Ba$_2$CuSi$_2$O$_6$ (lightblue).

This seems to be of considerable advantage for the Egyptian manufacturer, but certainly caused difficulties to those Chinese manufacturers trying to synthesize pure tones. On the other hand it was an advantage for those Chinese painters, who wished to vary their tone of colour from blue to purple in mixtures (colour plate XV, fig. 5).

The Chinese applied the Egyptian Blue analogue BaCu$_2$Si$_2$O$_6$ and the purple phase BaCu$_2$Si$_3$O$_9$. These phases differ in colour strength and tone, e. g. the Chinese painter was able to enlarge the spectrum of his blue colour palette by using or admixing one or the other purplish or bluish phase. Of course the choice was limited with respect to the skills in fabricating pure phases.

The synthesis of the pure phases is not direct: depending on the raw materials used, their ratio, the addition of fluxes and of course the temperature, atmosphere and reaction time different products, but usually a mixture of compounds is obtained. Since the Chinese civilization was very adept at functionalizing natural minerals, it seems of special interest, which resources for barite were used: Barite, BaSO$_4$, is found in a variety of deposits all over China, or Witherite, BaCO$_3$, which is much rarer and sometimes associated with barite. As will be shown the choice between these minerals can be quite relevant for the products obtained by the available techniques. It is very likely that copper-sulfides were used together with barite and silica sand or quartzite. Thus, one can assume that the copper minerals for the fabrication of the blue and purple BaCu-silicate pigments e.g. used in the Mogao Grottoes were collected in deposits of the Gansu province, e.g. near Lanzhou, Gulong or Jiayuguan (Gloria, 1985). Our experimental studies focused on the effect of the barium mineral used. As copper source tenorite, CuO, was used, since any copper sulfide is oxidized to CuO well below the temperature where the reaction starts (Bayer, 1992). The parent materials BaSO$_4$, BaCO$_3$, CuO, Cu$_2$S, SiO$_2$ were homogeneously
mixed and slightly compacted. Heating times at the various temperatures were usually 20 hours. The identification of the crystalline reaction products was done by X-ray diffraction. The influence of fluxes such as NaCl, Na₂CO₃, and PbO (found in various pigments) were studied. Additional investigations were concerned with the thermochemical reactivity of the various pigment samples. Previous studies on BaCu₅Si₃O₁₀ blue confirmed that there is a distinct effect not only of the temperature used but also of the Ba-compound and of the fluxes added on the colour tone of this pigment (Bayer, 1976).

Mixtures of BaCO₃, CuO, and quartz powder were prepared with different stoichiometric ratios (1/1, 1/2, 1/1/2 and 2/1/2). The mixtures were filled in porcelain crucibles, slightly compacted and heated at 900, 1000 and 1100 °C in air. To some of these mixtures 3% Na₂CO₃ or 5% PbO or 10% NaCl were added as a flux. TG-DTA runs of 1/1 and 1/1/2 mixtures showed that, owing to the presence of SiO₂, the decomposition of BaCO₃ already starts below its phase transition at around 800 °C (Wiedemann, 1986; Wiedemann, 1992). The decomposition to BaO + CO₂ proceeds faster above this temperature and is complete at about 950 °C. The solid state reaction to Ba-Cu-silicates probably starts around 900 °C. Depending on the BaO/CuO/SiO₂-ratio partial melting and reduction of Cu⁺ to Cu⁺ occurs at temperatures above 1050 °C. The purple compound BaCu₅Si₃O₁₀ is formed as the primary Ba-Cu-silicate, also in mixtures with the stoichiometry 1/1/4. It is thermally less stable than BaCu₅Si₃O₁₀ and melts with decomposition around 1100 °C.

As mentioned above, the addition of fluxes have a definite effect on the formation and the colour of the pigment. Pure Ba₅Cu₅Si₃O₁₀ can be synthesized by adding fluxes such as Na₂CO₃ or borax. The addition of more than 5% Na₂CO₃ and heating above 1000 °C resulted in the melting of the purple BaCu₅Si₃O₁₀ compound to a glass. However, the fluxes may also cause side reactions. Addition of NaCl causes volatilisation of some copper as CuCl₂ and disproportionation to CuO in the cooler zone of the furnace. In starting mixtures where BaCO₃ is present as the barium source, the addition of Na₂SO₄ causes the intermediate formation of Ba₅SO₄ due to the displacement reaction BaCO₃ + Na₂SO₄ → BaSO₄ + Na₂CO₃ in the temperature range of 600 to 800 °C (Bayer, 1987). Fluxes such as Na₂CO₃, PbO or borax did not cause problems. Since many original Chinese Purple pigments contained a high proportion of lead oxide, this oxide was also tried as a flux. It was found to be very effective in the formation of both Chinese Purple and Chinese Blue already at 900 °C. However, additions of more than 5% PbO led to partial melting and glass formation above 1000 °C (Wiedemann, 1997a and b).

In addition to their function as flux, lead additives can activate BaSO₄. In the presence of lead oxide (or carbonate) a dismutation reaction with barite can be envisaged, which leads to equilibrium formation of lead sulfate PbO + BaSO₄ ↔ BaO + PbSO₄

Since pure lead sulfate decomposes at around 1000 °C to PbSO₄ + 2 PbO (Malinowski, 1996), much lower than BaSO₄, which decomposes at 1560 °C, it can be anticipated that the BaO will be withdrawn from the equilibrium by the Chinese Blue or Purple formation, while the PbO part will be reintroduced into the barite decomposition process. Thus, lead additives can also take over the function as a catalyst for the decomposition of BaSO₄, at comparatively low temperatures, which is a decisive circumstance especially for the preparation of the thermally less stable Chinese Purple.

When copper sulphide minerals are used as starting material, their oxidation leads to the evolution of SO₂, which reacts with BaCO₃ to BaSO₄. Compared to a parent mixture of identical stoichiometry where CuO is used instead of e.g. Cu₂S distinct changes of the colour tone of the product are observed. In both cases, however, Chinese Purple (1/1/2) and Chinese Blue (1/1/4), as well as mixtures of both can be identified by X-ray diffraction. Obviously the presence of BaSO₄ changes the synthesis pathway of the different phases: BaSO₄ has a higher thermal stability and starts to decompose under the reaction conditions only slowly above 950 °C. As thermogravimetric measurements proved a large amount of BaSO₄ does not react even after heating for 20 hours at 1100 °C. Therefore the ratio between the reaction products BaCu₅Si₃O₁₀ and BaCu₂Si₃O₁₀ and hence also the colour tone differs from that of corresponding mixtures using BaCO₃ as barium source (Wiedemann, 1997b).

The slower decomposition rate of BaSO₄, mobilising only small amounts of BaO obviously favours the primary formation of the silica-rich Chinese Blue, BaCu₅Si₃O₁₀. Even for 1/1 starting mixtures and at 1100 °C BaCu₂Si₃O₁₀ continues to persist besides Chinese Purple, BaCu₅Si₃O₁₀. This is in contrast to the corresponding starting mixtures containing BaCO₃, where the formation of Chinese Purple is strongly favoured and where reactions generally start at lower temperatures.

The fact that we have the possibility to investigate blue copper pigments as test material on the technological skills of ancient Egyptian and Chinese manufacturers also accounts for the chemical stability of these synthetic and simultaneously aesthetic products. It could be shown that the silica-rich phases Egyptian Blue, Ca₅Cu₃Si₃O₁₀ and Chinese Blue, Ba₅Cu₃Si₃O₁₀ adopt analogous structural frameworks. As the X-ray diffraction confirms, there is also a Sr₅Cu₃Si₃O₁₀ analogue, which seems to be present in certain archeological samples (Sistrum and Goblet Hasanlu, Iran of Table 1).

Physical Investigations of Ancient Egyptian Blue, Chinese Blue and Purple Samples

Methods of Characterization for Ancient Pigments

Ancient pigment samples often appear as heterogeneous mixtures and due to this varying content of the pigment are present in coloured materials. Apart from this, the pigments themselves may have differing compositions based on the fact that they might consist of more than one similar, but distinguishable chemical species. Quite often the origins of this are complicated phase diagrams of such materials, which make it difficult to define appropriate conditions in the synthesis of a peculiar species. Accurate analyses of multicomponent heterogeneous mixtures constitute challenging problems in chemistry, especially in view of the fact that the analyses are expected to be carried out in a nondestructive fashion applying samples in the milli- or microgram range.

In recent years however, physicists and chemists have developed an arsenal of very powerful, sophisticated methods for the detailed investigation of ancient materials. In particular miniaturization, utilization of new physical effects and advanced computerization have contributed to an enormously improved situation, which allows us to obtain satisfying information on the na-
ture of such mixtures. Important applicable methods typical of
the analysis of compact and powdery samples are:

A) Thermal analysis

Most widely used in this area are thermogravimetry (TG) and
differential thermal analysis (DTA) with its frequently used
branches of differential thermal gravimetry (DTG) or dif-
ferential scanning calorimetry (DSC), which allow characteriza-
tion of materials through their physical and chemical behaviour under
the influence of temperature.

B) Scanning Electron Microscopy (SEM) and Energy
Dispersive X-ray analysis (EDX)

Applied to ancient samples SEM is superior for their surface
characterization and studies of their macroscopic fine structure
(e. g. texture, surface appearance and composition etc.). EDX is
used in combination with electron microscopy and provides rea-
sonable estimates of elemental compositions in the surface
regime of materials.

C) Powder X-ray diffraction

A useful method to determine and identify single components in
heterogeneous mixtures by their characteristic powder X-ray
diffraction patterns.

D) IR and Raman spectroscopy

Raman and IR spectroscopy are (sometimes complementary)
 vibrational spectroscopy methods. Dealing with solid samples
Raman spectroscopy is superior to IR spectroscopy. Usually it is
applied in combination with a microscope and allows easy iden-
tification of mixtures of phases according to the vibrational pat-
terns of the atoms in the microscopic structures of unique
components.

E) UV/Vis spectroscopy and laser induced photoluminescence
(PL)

Both methods support the characterization of chromophores of
pigments or dyes.

In the following section the described methods are applied to
a selection of samples of Table 1.

A) Thermal analysis of Egyptian and Chinese Blue and Purple

In conjunction with Egyptian Blue and Chinese Blue and Purple
preparations TG or DTA methods have been used for the pursuit
of the solid state reaction courses. Figure 9 shows in an exem-
plary way the TG curve for the formation of Egyptian Blue from
Malachite (Wiedemann, 1986).

First we see the decomposition of Malachite between 300 and
400 °C to produce CuO. At approximately 550 – 740 °C CaO
and CuO react with SiO₂ in the presence of the flux to generate
CaCu₅Si₄O₁₄, Egyptian Blue. Similarly, the solid state reaction
between azurite, calcium carbonate and sand also leads to
Egyptian Blue.

The synthesis of Chinese Blue was similarly studied by
TG and DTG in fig. 10 starting from BaCO₃, quartz and
CuO.

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colour appearance. For example, in figure 11 DSC curves of a contemporary Egyptian Blue and ancient Egyptian Blues of Table 1 are shown, which demonstrate by their quartz peak (and partly by their calcium carbonate peak), residual contents of these starting materials, which would even allow quantification (Wiedemann, 2001).

![Graph showing DTA curves for selected Egyptian Blue samples as designated. The left peaks correspond to the quartz transitions (see text) and the right ones to the decompositions of CaCO₃.](image)

**Fig. 5.** DTA curves for selected Egyptian Blue samples as designated. The left peaks correspond to the quartz transitions (see text) and the right ones to the decompositions of CaCO₃.

图 5. 选定的埃及蓝样品的差热分析曲线。左边的峰对应于石英转变（见文章内容），右边的峰对应于 CaCO₃ 分解。

Thermal analysis investigations of contemporary synthesized Chinese Blue lead to very similar conclusions as for Egyptian Blue (Wiedemann 1997 a and b), e.g. that residual quartz contents are expected to be traceable even in ancient samples. Whether this conclusion is valid for Chinese Purple, as well, is unclear. A respective study was attempted on the ancient Chinese Purple Freer Gallery stick which by Raman spectroscopy was claimed to contain some SiO₂. However, the assignment of the Raman band of quartz is ambiguous, since in the range of 460 cm⁻¹ it may be obscured by the presence of a weak band of Chinese Purple appearing at approximately the same wave-number. DSC measurements did not reveal a quartz peak. This may be attributed to the possibility that there is indeed no quartz present. An alternative interpretation could be based on the relatively high reactivity of BaCu₃SiO₆. At the given temperature the excess quartz reacts further with Chinese Purple to give Chinese Blue in an almost thermoneutral fashion according to the equation:

\[ \text{BaCu}_3\text{SiO}_6 + 2 \text{SiO}_2 \rightarrow \text{BaCu}_3\text{Si}_2\text{O}_9 \]

Thus, Egyptian and Chinese Blue samples may be analyzed by DSC for residual quartz contents (also for CaCO₃ and perhaps even for BaCO₃). However, when applying DSC for excess quartz studies of Chinese Purple, it is not clear yet, whether reliable conclusions can be drawn.

**B) Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX)** of samples of Egyptian Blue and Chinese Blue and Purple

In this section it will be demonstrated that the combined techniques of SEM and EDX applied to the Egyptian and Chinese samples such as indicated in Table 1 are very beneficial for the elucidation of surface structures of pigments and their elemental compositions. Figure 12 clearly shows two electron micrographs of two samples of the crown of Nefertete and of stick 4070, which reveal a platelet-like microcrystalline structure of the Egyptian Blue and the Chinese Purple content.

Table 2 and 3 contain valuable EDX microsonde type applications for the determination of the elemental composition of ancient pigment surfaces. A statistical approach was used with measurements at different surface locations in order to average local deviations. Interpretation of these values lead to the following conclusions:

The investigated Egyptian Blue samples show grossly constant composition over time, which is surprising, especially in view of the great period of time which their origins span. Regarding the average values of all samples, in comparison with the theoretical composition of Egyptian Blue CaCu₃SiO₆, the ideal values for calcium and copper were usually underscoring by the Egyptian producers, while the amounts of silicon were always too high. This is confirmed by the results of the thermanaliticaly studies (vide supra) and of the Raman investigations.

![SEM photograph of sample crown of Nefertete (above) and Stick 4070 (below) revealing crystallinity and the platelet-like structure of both samples.](image)

**Fig. 6.** SEM photographs of sample crown of Nefertete (above) and stick 4070 (below) revealing crystallinity and the platelet-like structure of both samples.

图 6. Crown of Nefertete 样（上图）和 Stick 4070 样（下图）的扫描电镜图，该图显示了两个样品的结晶性及其类片状结构。
Table 2. Composition of Egyptian Blue samples from different periods.

<table>
<thead>
<tr>
<th>Time</th>
<th>Period</th>
<th>Composition, [%]</th>
<th>Objects</th>
</tr>
</thead>
<tbody>
<tr>
<td>2575-2134 B.C.</td>
<td>Old Kingdom</td>
<td>Ca: 15.2, Cu: 21.3, Si: 63.0</td>
<td>Mereruka, Saqq. Egypt</td>
</tr>
<tr>
<td>2040-1640 B.C.</td>
<td>Middle Kingdom</td>
<td></td>
<td>Tomb Intef, Egypt</td>
</tr>
<tr>
<td>1340 B.C.</td>
<td>New Kingdom</td>
<td></td>
<td>Neferete, Berlin, Germany</td>
</tr>
<tr>
<td>1353 B.C.</td>
<td>New Kingdom</td>
<td></td>
<td>Echnaton Temple, Blue of Talatat</td>
</tr>
<tr>
<td>712-332 B.C.</td>
<td>Late Period</td>
<td></td>
<td>Bes Amulet, Egypt</td>
</tr>
<tr>
<td>332 B.C. – 395 A.D.</td>
<td>Greek-Roman</td>
<td></td>
<td>Mummy Coffin</td>
</tr>
<tr>
<td>13th-7th Cent. B.C.</td>
<td>Mesopotamia</td>
<td></td>
<td>Brick Nimrud, Iraq</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Average of all samples</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ca: 16.0, Cu: 22.7, Si: 60.4</td>
<td>Egyptian Blue, theoretical</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Compositions of Chinese stick samples with respect to major constituents [weight or atom % (in brackets)] from EDX. Other elements of minor amounts add up to 100%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca (g)</th>
<th>Ba (g)</th>
<th>Cu (g)</th>
<th>Si (g)</th>
<th>Pb (g)</th>
<th>S (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freer Gallery</td>
<td>2.5</td>
<td>35.3</td>
<td>5.6</td>
<td>37.7</td>
<td>11.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Stick 4069</td>
<td>3.1</td>
<td>31.6</td>
<td>13.2</td>
<td>15.8</td>
<td>35.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Stick 4070</td>
<td>1.0</td>
<td>36.5</td>
<td>15.6</td>
<td>25.9</td>
<td>20.7</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Not analyzed due to a too high amount of lead*

Table 3. The Ba/Cu atomic ratios are however approximately 1:1. Quite counterintuitively, stick 4069, which consists of an approximate 1:1 mixture of Chinese Blue and Purple with silica-rich Chinese Blue (see also powder X-ray studies) possesses less Si atomic content than stick 4070. This contradiction can only be reconciled with the assumption that stick 4070 additionally contains quartz or other quartz-rich compounds.

The sticks also contain non-Purple or Blue constituents in greater quantities. As already noted in earlier research (FitzHugh, 1992), they are often mixtures of compounds and also consist of calcium in quantities > 1% and great amounts of lead. While calcium with its relatively low content can safely be identified as an unintended ingredient accompanying starting materials from sand, Barites or Witherite, the lead content is of chemical relevance and was added as an essential ingredient to all the ancient Chinese pigment preparations (vide supra). The amount of lead in stick 4069 is especially high, even exceeding 30% in weight (Table 3).

Minor constituents of the sticks are: Freer Gallery stick: Na, K, Al, Fe, Cd and S, Cl; stick 4069: Al, Fe, Cd; stick 4070: Al, Fe. It should be noted that stick 4069 presumably also contains sulphur, which could not be analyzed by EDX due to overlap with a too intense lead X-ray emission. Quite remarkable are the cadmium contents of the Freer Gallery stick and of stick 4069. Because of the uniqueness of this element in the blue and purple pigment content, its presence may point to a common mineral or even synthetic origin. The nature and function of the chloride content of the Freer Gallery stick is still puzzling. It was supposedly introduced as NaCl or KCl. The accompanying amounts

(vide infra), which in several samples show the presence of residual quartz. The "clearest" Egyptian Blue is contained in the sample of the Neferete bust, which is in all constituents quite close to the theoretical values. The greatest deficiency is given by the Mesopotamian Brick Nimrud, which deviates by more than 10% in calcium and more than 16% in copper. Intriguingly it shows a high amount of quartz. An interpretation of this observation would be that the brick presumably was designed as a sophisticated construction material, which required specialized material properties and consequently a different chemical composition.

Deviations from the ideal compositions of Egyptian Blue may in general arise from inclusions of the flux material, starting materials or furthermore from influences of the matrix, in which the pigments were embedded. Quite often this is seen by the appearance of additional elements in the compositional analysis. For instance the samples of the Neferete bust contains the metal ions of Na, K, Mg, Al, Fe and Ti and the non-metal elements S and Cl as minor constituents. Similarly, the Talatat and the Bes samples have traces of K, Mg, Al, Fe and S, Cl and Al, Fe and S, Cl. The Ptolemaic sample consists additionally of zinc, besides traces of K, Ti, Fe and Cl. The zinc content is also found in certain Raman bands not identified in other Egyptian Blue samples. Zinc is therefore a unique companion of ancient Egyptian Blue samples. Its origin and possible function is yet unclear. It should be noted in this context that tin has been frequently found in original samples of Egyptian Blue (Jaksch, 1983).

The ancient Chinese samples analysed by EDX do not show clear-cut atomic ratios with respect to BaCuSi_2O_6 or BaCuSi_2O_5 (Table 3).
of aluminium are presumably in all samples of impure quartz as a starting material, which was very likely used in the synthesis as crude sand.

From the Freer Gallery stick the octagonal plate, shown in colour plate XV, fig. 2, was investigated in greater detail. It reveals a porous but otherwise hard and compact surface. It can be divided into a darker central core and a lighter fringe section. Magnifications of these areas by SEM show qualitatively no difference in the heterogeneous microcrystalline surface morphology of the core and the fringe areas. Both sections have obviously darker pigment areas and lighter inclusions (fig. 13).

Based on the areal dependent EDX analysis a schematic profile of the major elemental constituents can be established (fig. 14).

In absolute measures the silicon content is very high, it even increases drastically from the outside to the inside of the sample. Similarly, but to a much lower extent the amount of sulphur increases, while the other elements of significance like Ba, Cu and Pb conversely decrease in this direction. Lead even reaches almost zero atomic content in the center. From the DSC measurements (vide supra) it seemed likely that there is no free SiO2 in this sample. The high silicon value can thus only be interpreted in terms of the presence of silicates (presumably mainly glassy Ba-silicates). Furthermore, it can safely be anticipated that sulphur appears as sulphates. Lead and barium sulfate should thus meet to a noticeable extent on the transition of the outer to the inner part (PbSO4) and in the center area (BaSO4). The “outside” lead is assumed to appear primarily as PbO (as confirmed by Raman spectroscopy). Finally it should be noted that the atomic copper content of this sample is quite low. In ideal Chinese Purple it is expected to be 25% considering the eutectic ingredients alone. Thus, in total copper not even half of the Ba content is reached. Nevertheless, as we shall later see, only Chinese Purple was definitely identified by Raman spectroscopy, so that the “excess” barium is not expected to be engaged in the formation of other barium-copper-silicate phases, such as Ba2Cu7Si3O18.

The amount of lead decreasing from outside to inside may be interpreted in terms of a specific preparation process for this stick. It may be assumed that, before reaction, the lead (as PbO or PbCO3) covered the reactants as a crust. (See also FitzHugh, 1992). At higher reaction temperatures the lead starts to penetrate the inner parts of the stick by diffusion. However, the lead did not apparently fully reach the center to the extent required for completion of the chemical processes. In the presence of lead, the described catalytic decomposition (vide supra) of the presumed major starting constituent BaSO4 is expected to be promoted producing Chinese Purple and volatile sulphur compounds. With this in mind the lead gradient would then also explain the sulfur profile increasing from outside to inside (see fig. 14). Not shown in the diagram is the minor constituent chloride, which appears only in the central area to a detectable extent. All the given observations make it reasonable to assume that the inner section consists more of non-purplish compounds, while the fringe area shows more of Chinese Purple. Contrary to the generally lighter appearance of the fringe section, Chinese Purple is apparently to a greater extent associated with the lead.

Judging from EDX studies, the Terracotta Army, samples I and II, indeed consists of the Chinese Blue and Purple constituents Ba, Cu and Si. As in the earlier investigations (Herm, 1995; Thieme, 1995) a relatively high Pb content was noticed (fig. 15). This could be related to its function as a synthetic additive, but could also point to its role as a pigment component in

Fig. 7. SEM of the Freer Gallery stick comparing the surface morphologies of the fringe (above) and the centre area (below).

Fig. 8. Schematic plot of the profile of the atomic content of Ba, Cu, Pb, S and Si in the slice of the Freer Gallery stick.

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As for the other elements present in the Freer Gallery stick, it can be noted that the silicon content is very high, which is typical for Chinese Purple. The sample was investigated in greater detail, revealing a porous but otherwise hard and compact surface. The stick can be divided into a darker central core and a lighter fringe section. Magnifications of these areas by SEM show qualitatively no difference in the heterogeneous microcrystalline surface morphology of the core and the fringe areas. Both sections have obviously darker pigment areas and lighter inclusions (fig. 13).

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form of PbO or PbCO₃ in mixture with Chinese Purple. Sample II contains, besides Chinese Purple, cinnabar, phosphorite or apatite and ilmenite, Fe₂TiO₅, representing red, white and brown colouring tones. The ilmenite and the phosphorus compounds were found as isolated pieces on the mm scale and could therefore be studied separately by EDX without a disturbing background. The EDX analysis revealed almost exactly the atomic ratios expected for Fe₂TiO₅ and Ca₃(PO₄)₂.

In particular, it is worth mentioning that the EDX analysis of

Several Egyptian Blue samples in Table 1 have been analysed and consist of prevailing CaCu₅Si₅O₁₆ according to the presence of the respective major Egyptian Blue reflections of Figure 16. Impurities could only be identified properly when they were contained as major constituents. This was the case for the strong quartz content of Brick Nimrud.

The Chinese samples, the Freer Gallery stick, stick 4069 and stick 4070 were analyzed by X-ray powder diffraction, as well. The pigment component of the Freer Gallery stick and of stick 4070 was Chinese Purple. Chinese Blue was not found to be present within detection limit. However, from the powder diffraction analysis of stick 4069, it could be derived that it consists of an approximately 1:1 mixture of Chinese Blue and Purple. The Freer Gallery stick shows the greatest amounts of impurities. They were identified as BaSO₄, PbSO₄ and BaCO₃. Several remaining reflections of this quite heterogeneous mixture could not be assigned, but are assumed to belong to certain crystalline areas of silicates.

The powder diffractogramme of stick 4069 contained minor reflections for BaSO₄ and PbSO₄, while that of stick 4070 displayed additional reflections for PbCO₃, (see fig. 17). A few reflections in each of the samples could not be designated.

D) Micro-Raman spectroscopy of original samples containing Egyptian and Chinese Blue and Chinese Purple

Micro-Raman spectroscopy can advantageously be used for the identification of pigments in heterogeneous mixtures like paints and paint applications. Concerning Barium-copper-silicate it previously has been applied only in the case of Chinese Purple (Finger 1989, see also McKeown, 1997). Our Raman studies on various ancient samples (indicated in Table 1) and reference samples brought about well-defined conclusions. In the spectral range of 1200 – 100 cm⁻¹ Egyptian Blue and Chinese Blue samples show two very strong Raman emissions between 1080 and 1090 cm⁻¹ and 1100 cm⁻¹, respectively, and around 430 cm⁻¹ for both types of species. In an exemplary way the Raman spectra of the Crown of Nefertite and the Amulet Bes are shown in figure 18.

The Chinese Blue bands at around 1100 cm⁻¹ are thus of little higher energy than the corresponding ones of Egyptian Blue, a fact which could be used for their distinction. The two major bands of the corresponding strontium blue SrCu₅Si₅O₁₆ would appear at 1090 and 425 cm⁻¹ very close to those of Egyptian Blue. In all the Egyptian Blue samples indicated in Table 1, we were thus able to identify Egyptian Blue by Raman spectroscopy. Major and dominant contents of impurities could be detected only in a few samples. For sample Pthah-Sokaris-Osiris, which consists of Zn according to EDX, this presumably is indicated by a very strong Raman band at 745 cm⁻¹. This band could, however, not yet be attributed to a certain chemical species. The Raman band of quartz (460 to 470 cm⁻¹) is especially strong in certain spots of the spectrum of Brick Nimrud and otherwise seen in the samples Ba-bird indicating medium amounts. In all the other Egyptian Blue samples there is only a very weak respective band. Unfortunately, the major Raman emission for CaCO₃ (1088 cm⁻¹) overlaps with the 1080 – 1090 cm⁻¹ band of Egyptian Blue so that the limestone content of original samples cannot easily be analysed. In agreement with the EDX results for sulphur, the Raman spectra of several Egyptian Blue samples revealed the presence of very small amounts of CuSO₄ (Mastaba of Merenuka, Tomb Intef, Bust of Nefertite, Amulet Bes, Mummy cartonage, Mummy coffin and Cylinder Seal, Thebes).

![Figure 9. EDX of sample I of the Terracotta Army displaying the major constituents Ba, Cu, Si and Pb and minor quantities of other elements as impurities.](image-url)

图 9. 兵马俑样品 I 的能量色散 X-射线分析, 结果显示样品主要成分是 Ba, Cu, Si 和 Pb 并含微量的其它元素杂质。
Fig. 10. Stick representations of the Powder X-ray Diffractograms of Egyptian Blue, CaCuSi₄O₁₀ (Cuprorivaille), Chinese Blue, BaCu₅Si₄O₁₀ (Effenbergerite) and Chinese Purple, BaCu₅Si₄O₁₀. Only the more intense reflections are given.

Fig. 11. Stick representation of the Powder X-ray Diffractogramme of Stick 4070. Lines not designated belong to Chinese Purple. o refers to major lines of PbCO₃.
*Not assigned.

Fig. 12. Raman spectra of original samples of Egyptian Blue (Excitation Laser 514 nm). Left the spectrum of the blue from the crown of Nefertete. Right the spectrum of the Amulet Bes. Both samples display primarily Egyptian Blue.

Fig. 12. 埃及蓝原样的拉曼光谱（激发光 514 nm）。左图为 Crown of Nefertete 样的光谱，右图为 Amulet Bes 样的光谱。两个样品都
From the Chinese samples, stick 4069 contains Chinese Blue, which however is is mixed with Chinese Purple (see fig. 19). This confirms the result of the powder X-ray studies.

Spectra of Chinese Purple samples revealed, as finger-print patterns, two strong bands at around 590 cm\(^{-1}\) and 514 cm\(^{-1}\). A band at 990 cm\(^{-1}\) could also be identified, but in contrast to the blue pigments this band at higher wave-numbers is only of medium intensity. Chinese Blue and Chinese Purple are thus easily distinguishable by Raman spectroscopy.

In all Chinese samples the following potential impurities were checked, which might originate from the minerals used, the added flux or chemical transformations occurring during synthesis: CuO, Cu₂O, azurite, BaCO₃, BaSO₄, PbCO₃, 2 PbO, PbSO₄, CdO and SiO₂. Several Chinese samples presumably show a Raman emission for quartz, which varies in relative intensity from sample to sample. However, identification of the Raman band of minor amounts of quartz in mixtures with Chinese Purple is obscured by the fact that Chinese Purple also possesses an emission of medium to weak intensity in this region. In the Raman spectrum of the Chinese sample, the Royal Ontario Museum stick, no definite conclusions on impurities could be drawn due to the low quality of the spectrum caused by an insufficient amount of sample. Stick 4069 showed quartz, however no spectrum of isolated spots showing BaSO₄ and BaCO₃ expected from the powder X-ray results could be found. Stick 4070 unambiguously showed the presence of PbCO₃.

As in the case of the EDX analysis, the slice of the Freer Gallery stick was investigated in greater detail by Raman spectroscopy. Table 4 shows the results of the Raman study at 12 different spots following an approximate order from outside to inside. In general the given collection of spectra makes clear that this stick is a very heterogeneous mixture, since several other components have been detected besides Chinese Purple.

Several bands were assigned to crystalline or glassy silicate phases. Other attributable phases were CaCO₃, BaCO₃, BaSO₄, PbSO₄, PbO and perhaps SiO₂. They are in full agreement with the elemental contents analyzed by EDX. Apparently due to some arbitrariness in the choice of the measured spots and the heterogeneity of the sample, an accurate areal dependence like that of the EDX analysis could not be established.

It is however clear that, due to the various residual constituents, it can be concluded that the stoichiometry of the starting materials did not match that of Chinese Purple. An insufficient copper content leads to production of several non purple constituents. Presumably the bands around 940 and 421 cm\(^{-1}\) account for glassy phases with polysilicate (SiO\(_2\)) units and the bands at 914 cm\(^{-1}\) for disilicate (Si\(_2\)O\(_5\)) (Frantz, 1995). Due to

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**Fig. 13.** Raman spectra of stick K 4069 at two different spots (Excitation Laser 514 nm). The spectrum above corresponds to Chinese Purple, the spectrum below to Chinese Blue with some impurity of quartz (464 cm\(^{-1}\)).

**Fig. 14.** Raman spectrum of sample 1 of the Terracotta Army (Excitation Laser 514 nm) displaying the spectrum of Chinese Purple with some impurity of PbCO₃.
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Table 4. Raman data of various spots (column) of sample Freer Gallery stick with assignments. CP = Chinese Purple. Weak bands in brackets; ? = not assigned.

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Table 4. Raman data of various spots (column) of sample Freer Gallery stick with assignments. CP = Chinese Purple. Weak bands in brackets; ? = not assigned.

the great stoichiometric excess of SiO₂ (see also EDX analysis) glass formation seems to be very plausible and indeed the relatively hard general nature of the disc speaks for a relatively high amount of glassy phases. It is maybe quite amusing to see that an early German patent from 1900 describes the preparation of glassy highly coloured barium-copper-silicates for use as pigments (Le Chatelier, 1900). This historic discovery was certainly made without knowledge of the existence of Chinese Blue and Purple and may simply reflect need for artificial colouring matter.

The Terracotta Army samples I and II consist of Chinese Purple as indicated by the appearances of the major Raman bands for this compound (fig. 20).

A relatively high PbCO₃ or PbO content was noted. This could be related to their function as synthetic additives, but could also point to their role as colouring components. For sample I and II cinnabar could be traced as indicated also by EDX. I and II also showed substantial quantities of matrix constituents, such as quartz. This is assumed to be a natural circumstance associated with their use in paints. It should, however, be noted that none of both samples showed the presence of Chinese Blue. Sample I possessed considerable amounts azurite crystallites (major Raman band at 402 cm⁻¹), which apparently stood for the blue colouring tone in the pigment layer. In contrast to the sticks, the Terracotta Army samples represent mixtures of actual paints, which are naturally more heterogeneous. Their a priori heterogeneity, however, makes it sometimes difficult to decide whether a specific component is to be attributed to a mineral or chemical origin or whether it was related to a colouring function.

<table>
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<th>CaCO₃</th>
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<th>CP/PbSO₄</th>
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Table 4. Raman data of various spots (column) of sample Freer Gallery stick with assignments. CP = Chinese Purple. Weak bands in brackets; ? = not assigned.

Table 4. Raman data of various spots (column) of sample Freer Gallery stick with assignments. CP = Chinese Purple. Weak bands in brackets; ? = not assigned.

E) UV/Vis and Photoluminescence spectroscopy (PL) of Egyptian Blue and Chinese Blue and Purple

As mentioned before, Chinese Blue and Purple contain copper(II) ions as effective chromophores. The electronic structures of chromophore models of Chinese Blue and Purple have been calculated by us in order to trace any difference in the absorption spectra expected for Chinese Blue and Purple (Density Functional Calculations). In an ideal square planar silicate ligand environment as in Chinese Blue, the copper ion should give rise to only one visible absorption in the orange, which is seen as the complementary blue colour (compare with the UV/Vis spectrum of Egyptian Blue (Ford, 1979)). For Chinese Purple, however, two visible electronic transitions are expected to appear. One causes an absorption in the orange with a blue complementary colour very much as predicted for Chinese Blue. The other transition occurs in the green, which then appears purplish with its complementary counterpart. Both electronic transitions indeed arise from the Cu-Cu bonding in this compound. The experimental verifications of these predictions are yet to be established.

Photoluminescence spectroscopy is to the certain extent a complementary method to UV/Vis spectroscopy. For instance, when irradiated by a green laser beam Chinese Blue and Purple very effectively transform this light into fluorescent infrared light between 800 - 1100 nm (Ajo, 2000). This means that when sun light shines on Chinese Blue and Purple, they not only give rise to a blue or purple colour perception, but additionally emit heat radiation. Whether or not this latter circumstance may have an
effect on human perception is not clear, and has to our knowledge not yet been investigated. The luminescence spectra of synthetic samples of Chinese Blue and Purple reveal that the fluorescent light of both is emitted as a characteristic double band pattern, where the shorter wavelength band appears as a less intense shoulder for Chinese Purple, while for Chinese Blue they have about the same intensity. The emission maxima of both compounds appear at somewhat different wavelength: 945 and 995 nm for Chinese Purple and 930 and 970 nm for Chinese Blue. The similarity of these emission bands with respect to their positions, and, to a certain degree, also to their intensities indicate that it is the copper($^{+}$II) ions that gives rise to luminescence. Unfortunately, this observation makes it impossible to use luminescence to identify and distinguish Chinese Blue and Purple in complex mixtures of both components.

Conclusions Drawn from the Chemical and Physical Investigations of Egyptian Blue and Chinese Blue and Purple

Our investigations gave clear evidence that the ancient Egyptian samples of Table 1 are all based on the chemical compound CaCuSi$_2$O$_6$, which is commonly denoted as Egyptian Blue. The samples of Table 2, investigated for their compositions normally deviate from the theoretical values. They show mixtures originating from their production process or from the fact that they were paint applications. A gross trend of constant compositions of the blue pigments can be recognized over a period of approximately 3000 years. This naturally required a stable route of transmission, that is, a reliable mechanism for the handing-down of the manufacturing recipe, which apparently could only be provided in the environment of a highly developed civilization.

Egyptian Blue was produced from quite abundant minerals. Only the copper component needed to be made available from mining sites. Copper mining was quite common at the time. It played a major role in the Egyptian civilization and also in previous human developments. The general situation of the resources did not impose restrictions on the spread of the use of Egyptian Blue. However, because of difficulties connected to the sintering-type solid state synthesis and the fact that Egyptian Blue cannot be processed by casting, technological restrictions emerged. Besides the general requirement that the minerals used for Egyptian Blue preparation required pretreatments like grinding and compacting, the production of compact blue bodies demanded specific sophisticated developments involving multistage processes. The physical and chemical conditions for successful production of Egyptian Blue were not too difficult and could usually be established with ease, such as the optimal temperature for the reaction, the temperature control and the maintenance of the reaction temperature over a longer period of time. Based on these circumstances the Egyptian pigment could be produced with satisfying quality over a great span of time.

For the Chinese pigments the general situation seems somewhat different. First of all it seems quite plausible that the production of Chinese Blue and Purple was based on the knowledge of the production of Egyptian Blue. Chemically the blue compounds resemble each other quite closely, and differ in the chemically minor variation of the replacement of calcium with barium. Such a variation is to be anticipated for ancient craftsmen, who were involved in purely empirical testing and did not have knowledge of atomic views and the Periodic Table of Elements. Nevertheless, it cannot be ruled out that the chemical developments for Chinese Blue and Purple occurred independently without any relationship to those of Egyptian Blue. This has to be stressed especially in view of the fact that there is no historical documentation concerning the ancient production methods of Chinese Blue and Purple in China. However, there are the two ancient artefacts, the Goblet and the Sistrum Hasulanu from Iran, which prove the spreading of the man-made blue into regions considerably east of Egypt. Secondly, it is indicated by these artefacts that chemical variations of Egyptian Blue occurred by modifying CaCuSi$_2$O$_6$ into at least partly the strontium derivative SrCuSi$_2$O$_6$. Both these facts provide further support for the hypothesis that the preparation of Egyptian Blue may have also become the basis for the development of ancient Chinese blue and purple pigments. The transmission of knowledge along the Silk Road, which also passed through Iran and which is anticipated to have been used as a trade route as early as 1000 B.C. To the present date we have to assume that Chinese Blue and Purple appeared no earlier than the Warring States period and that for this reason, these Chinese pigments are ‘younger’ than Egyptian Blue. They emerged in historic times when the Silk Road was in full operation as a trade path and concomitant with this as a potential path for the exchange of ideas.

Even if they were based on the knowledge of Egyptian Blue, development of Chinese Blue and Purple faced several difficulties. Firstly there was the mineral problem, that barium minerals are much rarer than those of calcium. Barite (BaSO$_4$) or Witherite (BaCO$_3$) display the prominent property of being heavy, which makes them recognizable in nature and perhaps because of this characteristic they caught the interest of eager human beings. In China barium minerals are not rare and thus it seems plausible that they were utilized. The other necessary ingredients for Chinese Blue and Purple production were abundant; SiO$_2$ used as quartzite or sand and copper as copper sulphide, malachite or azurite. Therefore, we can hypothesize about the actual synthetic procedure. The use of barite demanded the addition of lead salts, such as lead carbonate or lead oxides. As we have seen, lead salts promote the decomposition of the quite stable barite and can also act as a flux additive. With the given combination of ingredients Chinese Blue and Purple could then have been obtained by a sintering-type process at temperatures between 900 and 1000 °C. It should be noted that this temperature is about 150 – 200 °C higher than that required for the production of Egyptian Blue. In the technically highly developed China of the Qin and Han time the achievement of such temperatures seemed to be no principal problem (Wagner; 1996). However, the severer synthetic conditions with respect to Egyptian Blue required more intense provisions concerning the construction of firing devices etc. Applying appropriate temperature conditions would have permitted a typical batch of Chinese Purple to have been finished within 10 – 24 hours, while the production of Chinese Blue presumably must have taken twice as long. It seems to be somewhat of a technological problem how these relatively high temperatures could have been maintained for a longer period of time within narrow limits. In order to obtain acceptable product results, the temperature control had to be quite accurate, presumably + – 50 °C for Chinese Purple. Efficient temperature controlling devices were to our knowledge not known in the Qin and Han period or earlier. Therefore, the accomplishment of a steady temperature level had to be a matter of empirical testing and the production had to be supervised by experienced personnel. Manufacturing of the thermally less sensi-
tive Chinese Blue would not have required such strict control. This compound could even have been brought to melt at least for a short period of time.

For Chinese Purple it was not possible to obtain a homogeneous melt and it therefore had to be produced by a sintering or pseudo-sintering process. By doing so, relatively dense compact bodies like the described sticks were efficiently obtainable, since the sintering temperature is only about 100 – 150 °C from the potential melting point of the pure compound.

As previously indicated, Chinese Blue and Chinese Purple could have been produced as unique components or as mixtures controlled by the addition of appropriate amounts of SiO₂ and by applying appropriate temperatures and reaction times. If mixtures of both were the desired product, this could however have been achieved easiest by grinding the pure components together. In this way it was possible for Chinese painters to have all tones from blue to purple available. It is evident that the sticks of Purple and Blue were essential components of coloration mixtures of paintings and sculptures, as the Purple was used in the case of the analysed samples of the Terracotta Army. As mentioned before it is probable that the sticks were trade items. Their use thus required that pigment particles were ground from the sticks and added to the paint or colouring mixtures.

Relating back to the physical studies of the original Chinese samples, these made clear that, except for stick 4070, all of them contained considerable amounts of impurities. Highly contaminated is the Freer Gallery stick which witnesses incomplete chemical reaction and by a Cu:Ba ratio even considerably below 1, the additional formation of presumably glossy silicate components. These observations point out that the sticks were not of optimum pigment quality. Nevertheless, the overall appearance of the sticks seemed to be satisfactory with regard to their colouration properties.

In view of the fact that the preparation of Chinese Blue and Purple are still nowadays sometimes not easy to tackle, the invention of Chinese Blue and Purple may be considered a fine chemical and technological achievement. It is indeed an outstanding example of how the level of science and technology, which is well-described for ancient China by Joseph Needham and his collaborators (Needham, 1976) may positively influence civilizations. For early Chinese Culture we thus may recognize a steady unbiased impetus for improvements accompanied by high civilization standards.

Acknowledgments

We are indebted to the following institutions for their donations of original samples of Egyptian Blue: Crown of Nefertite: Ägyptisches Museum der Staatlichen Museen Berlin, Germany, Preussischer Kulturbesitz. Ptah-Sokaris-Osiris: Staatliche Sammlung Ägyptischer Kunst, Munich, Germany. Ba-bird: Kestner Museum, Hannover, Germany. Brick Nimrud: Laboratory of the British Museum of London, London. Great Britain.

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埃及与中国的蓝色及紫色的化学和物理研究

本文叙述了11个古代埃及蓝(CaCuSi₂O₆)颜料样品和6个中国蓝(BaCuSi₂O₆)的中国颜料样品的物理-化学研究。所有这些古代颜料都对应于固定的化学物质并通过化学合成方法得到。文章对这些化合物的化学进行了广泛的综述。尤其对它们的化学结构进行了讨论。其结构表现为无限连接的Si₃O₁₂⁴⁺单位的层状结构或含有孤立硅酸根环的[Cu₂Si₂O₆]单元的层状结构。结构的埃及蓝和中国蓝含有作为发色体的正方平面的Cu²⁺离子。中国紫表现很特别的Cu-Cu 链合的现象。这些化合物的稳定性依赖于它们的化学结构。埃及蓝和中国蓝很稳定，而中国紫化学和物理性质常易变。这一点归因于孤立硅酸盐环和Cu-Cu 链的存在。

文章详细叙述了这些化合物的现代及古代的制备方法，包括合成的物理及化学条件。着重阐述了在制备中国蓝和中国紫中铅化合物添加剂的作用。

用热分析、扫描电镜、粉末X-射线衍射、拉曼光谱、光致发光光谱对样品进行了表征，明确了样品的元素及物相组成。从而确定了制备这些颜料的原料、添加剂及制备条件。

跨越3000多年的不同时期的埃及蓝具有相对稳定的路线。中国颜料的合成需要更严格的物理和化学条件，这些条件更加难以满足。在这种情况下，中国蓝和中国紫的制备方法被假设为是建立在更古老的化学相关的埃及蓝的制备方法的基础上。不管怎样，中国颜料的精细化学品的成就也需要进一步发展。
中国漆树及应用

一、源远流长的中国生漆
漆本作漆，其字象汁自木出面滴下之形也(东汉许慎《说文解字》)。乃依推测，有区域形文字之前，也就是大约远在4000年前，我们中华民族对漆树和生漆就有了一定认识和应用。例如远在舜禹时代就用生漆涂饰食具和祭祀，西周时用生漆涂饰车辆，并征收过漆林税(《周礼》)。
《韩非子·十过》：“尧禅天下，授舜受之，作为食器，斩山木而财之，销熔其迹，流漆墨其上，输之于官，以为食器。……舜禅天下，而传于禹，禹作为器，墨漆其外，而朱画其内。”
《诗经·周南》：“山有枢，山有漆，隰有栗。”
《尚书·禹贡》：“兖州（今山东兖州）厥贡漆丝，豫州（今河南）厥贡漆皮……”
《史记·孔子世家》：“庄子者，蒙(即今中牟)今河南商丘附近，非今河南商丘人也，名周，周尝为蒙漆园史。”
《史记·货殖传》：“陈留千户漆，此其人与知府等。漆千斗(言满千斗，即今千桶也)，此亦为千乘之家，千乘之家，即千户之君也。”
《周礼》：“县(县官职名)掌任县之法，近郊十里，远郊廿里，九甸，甸，县，野，井田制：四邱为甸，四甸为县，四县为郡，四郡为国，皆有乡数，全乡之封，廿里五。”
以上文字材料足见中国古代对漆的认识和应用历史悠久，下面的考古发掘更能说明我国应用漆的历史的辉煌：四川成都羊马山172号战国中期墓，陕西省长安县普渡村西周墓；河南省洛阳市山陕庙沟西周墓，江苏省吴江县梅堰的新石器时代遗址；山东省临淄区牛家东周墓；湖北省江陵县望山，湖北省南台山，南台山等地相继出土一批战国时代的漆器；河北省蓟南县十缎台等村西周遗址；辽宁省辽河大甸子古墓，距今3400-3600年；山西省襄汾县陶寺遗址；北京房山县琉璃河；安徽省屯溪，浙江省余姚县河姆渡村遗址及在泰班马俑二号坑发掘彩绘兵器有生漆涂层等等；上述十余省(市)在对秦以前的考古发掘中均有发现漆相关的器物。

二、中国漆树及其分布
全世界漆属植物约25种，分布于亚洲东部和北美到中南美。中国产15种，主要分布于长江以南各省区，中国用来采集生漆的仅1种2变种(猕猴桃漆树)和漆树农家栽培品种，根据全国的调查近100个。迄今未发现有漆树属其他种进行割漆生产。在越南有野漆(Toxicodendron Succeedaneum)漆液，也可作涂料，被称为安南漆。在柬埔寨，泰国，缅甸和租借，植物为柬埔寨漆树Melanorrhoea laccifera，缅甸漆树M. usitata。鸡腰果Anacardium Occidentale的果壳中提取的果液，用于合成漆

涂料，中国海南、广东也把它用作涂料，应该说不属生漆的范畴。肖育模对中国现代漆树的地理分布进行研究的结果认为：大体符合中国植被区划中的暖温带落叶阔叶林区到中亚热带常绿阔叶林区（图1）。这个分布范围相当于北纬25°-41°46′，东经95°30′-125°20′，东西约1300公里，南北约900公里。按我国行政区划来说，包括了22个省区(市)的500多个县。其中以山西，湖北，四川，重庆，贵州，云南，甘肃，河南漆源最多。全国主要漆源县(市)和在100吨以上的如下：

| 省份 | 产量
<table>
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<tr>
<td></td>
<td>100-500 吨</td>
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<tr>
<td>陕西</td>
<td>留坝、商南、周至、南郑、凤县、太白、柞水、安康、旬阳、旬阳，镇安</td>
</tr>
<tr>
<td>湖北</td>
<td>房县、竹山、巴东、宣恩、鹤峰、神农架</td>
</tr>
<tr>
<td>四川</td>
<td>西昌、平武、南江、南充、合川、彭水、武隆、叙永、古蔺、开县</td>
</tr>
<tr>
<td>贵州</td>
<td>遵义、黎平、黔江、织金、铜仁、清镇、德江、务川</td>
</tr>
<tr>
<td>云南</td>
<td>东川、大关、威信</td>
</tr>
<tr>
<td>甘肃</td>
<td>天水、康县</td>
</tr>
<tr>
<td>河南</td>
<td>西峡、卢氏</td>
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图1. The distribution of lacquer trees in China.
Shang Zongyan, Zhang Jizu and Li Rujuan

The Chinese Lacquer Tree and its Use

China is a country with the greatest lacquer tree population in the world and its output of raw lacquer accounts for over 80% of world production. The raw lacquer, a quality natural paint, has been eulogised as "the king of paints". The history of using lacquer in China may date back to very ancient times. The legend goes that when the monarch Yao in the Patriarchal Clan Society was in power, he had wood cut, shaped and lacquer applied to its surface to make cooking utensils. Later Yao abdicated and handed over the crown to Shun, who inherited the lacquer wares and used them as sacrificial utensils. As Han Feizi (a philosopher in the Warring States Period) wrote in his book Shiguo, the utensils were "lacquer black outside and decorated with pictures inside". There have been many records in the classics about lacquer trees as to their place of origin, the plantation and management, the collection of lacquer, the taxation, etc. Lacquer trees are to be found approximately between 25° to 46° North Latitude and 95° to 125° East Longitude, covering 21 provinces (cities and autonomous regions) such as Shaanxi, Sichuan, Hubei, Guizhou, Yunnan, Hunan, Henan, etc. Of these places, Shaanxi is number one in the output of raw lacquer and its output of raw lacquer is one third of the total in China.
敦煌莫高窟的彩绘塑泥及其保护

前言

敦煌莫高窟的492个洞窟中，保存着从北凉(公元4世纪)到元代(公元14世纪)十一个朝代，延续千多年的2000多身彩绘塑泥。

这些彩绘塑泥其制作工艺大体分两类，其中小型彩塑，先以木制做骨架，再做泥塑，大型彩塑以石胎为骨架。

莫高窟的彩塑包括敷彩、泥塑敷彩在各个朝代都具有不同的特征，十六国、北魏等早期的敷彩比较简单朴素沉着，颜料主要用土红、石绿、石青、白、黑等。隋唐时代，莫高窟的泥塑彩绘发展到了光耀灿烂的时期，彩雕富丽堂皇，许多部位装金。特别是盛唐时期，彩塑的肤色大量应用于铅丹(PbO₂)和金箔，由于铅丹的严重变色，这个时期彩塑的肤色全已变得深棕色或深咖色。五代、宋代等时期，彩塑的敷彩比较素雅。到了清代，将早期的彩塑进行了重塑和重绘，敷彩的白色颜料大部分采用石膏，颜料为群青、白色颜料为白粉。

千百年来，由于受温湿度的变化，降水量，岩体透水，岩体和泥层中可溶盐的活动等环境因素的影响，莫高窟的彩绘塑泥不同程度的产生了各种病害。主要有彩绘颜料的变色、褪色；彩绘颜料层的龟裂变形；彩绘层的酥碱粉化；木骨架因变形引起的塑像肢体断裂或塑像倾倒；石胎岩体风化而导致的泥层剥落等。

对彩绘塑泥的保护修复采取了如下的方法和措施，倾倒彩塑的扶正、定位、加固：凿去木骨架脱落的泥质骨修复；风化石胎骨加固；酥碱、起甲颜料层加固修复；以及洞窟环境的治理，如洞顶洞窟顶加固和岩体裂隙灌浆以防止渗水。进行观景体验时对壁画、彩塑造成影响的环境监测和分析研究。控制每个洞窟参观人数，以免洞窟内CO₂和水份的剧增造成对彩绘颜料的影响。

1. 莫高窟彩塑的制做工艺

莫高窟的彩塑约有高达30多米，小的也有10多公分。其中小型彩塑，先以木料做骨架，然后在木骨架上裱扎发肤草或芦苇草做成人像的大体结构形象(图6)，再敷彩画泥，最后在表面塑以细绢画层。而大型塑像，不做木骨架，而是在开洞窟塑时，预留塑像石胎，将石胎泥塑成塑像的大体形状，然后在石胎上凿孔插槽，再在上面敷彩画泥，最后在表面塑以细绢画层(图6，2)

莫高窟塑像的木骨架是用当地的胡杨、杨木或柳木做成的，因为这是本地最普遍的几种树种，材质较坚硬。塑造的粘土是附近河床的沉积粘土或山洪暴发后在低洼地沉积的粘土。这种粘土细腻，大部分的可溶盐已被淋洗，吸水性小。泥层中掺加的草主要是麦草，细泥中掺加的纤维主要是麻或棉。

2. 泥塑的彩绘

莫高窟的泥塑彩绘全部敷彩。泥塑敷彩在各个朝代都有不同的特征，特别是敷彩所用的红色颜料，更具有鲜明的时代特征。十六国、北魏、西魏及北周等早期的敷彩比较简朴沉着，红色颜料主要以土红(Fe₂O₃)为主(彩图6V, 4)。土红在红色颜料中最稳定的一种，千百年来，这些彩绘的土红颜料没有发生变色，只是处于不同环境中的彩绘层中因含水不同，或者由于添加在颜料中的胶结剂老化程度不同，而颜料的亮度、彩度有所差异。

早期彩绘所使用的颜料的主要色是石膏(CaCO₃)和金箔(PbO₂)，和青铜器(SnO₂，Cu₄O₆)。绿色颜料主要是石绿(Cu₂O₂CuO(OH)₂)和蓝铜矿(Cu₄O₆Cl₂)，这些蓝色颜料和绿色颜料其化学性能较稳定，和上述相同的原故，其亮度和彩度有差异。彩绘的白色颜料主要是方解石(CaCO₃)，高岭土(Al₂Si₂O₅(OH)₄)，滑石(Mg₃Si₄O₁₀(OH)₂)。

隋唐时代，莫高窟彩塑的敷彩发展到了光辉灿烂的时期，敷彩富丽堂皇。彩绘所用的红色颜料主要是朱砂(HgS)和铅丹(PbO₂)，土红颜料明显减少。

朱砂是一种较稳定的红色颜料，由于长期受光照的作用，朱砂的晶状质产生了变化，部分由原来鲜艳的朱砂变成暗红色的黑晨砂。这仅仅是一种物理状态的变化，色相没有变化，亮度和彩度却发生非常明显的变色。

但是，由于受温湿度的影响，特别是开挖洞窟的初期，以及塑像所做成后高温高湿的环境作用，彩绘的铅丹基已变成棕褐色的二氧化铅(图1)。因此，这个时期的彩绘，凡用铅丹的部位，主要是肤色，基本已变成棕红色或暗红色的二氧化铅(彩图6XI, 3, 5)很难找到朱砂色的铅丹。这个时期彩绘所用的兰色颜料、绿色颜料以及白色颜料和早期彩绘所用的兰、绿、白颜料基本相同，另外，这个时期彩塑的服饰、菩萨项圈等部位装金，以显富丽。

五代，宋代等晚期，莫高窟彩塑的敷彩较清雅，这个时期的彩绘所用的红色颜料除土红外，大量采用了土红与铅丹，或朱砂与铅丹的混合红色颜料。铅丹与土红、或铅丹与朱砂混合后具有较稳定的化学性质，混合红色颜料中的铅丹基未变色，其原因不清楚，正进行化学机械的研究(图2)。这个时期彩绘所用的兰色颜料、绿色颜料和白色颜料基本与早期和隋唐时期所用的兰、绿、白色颜料相同。

清代，莫高窟的彩塑大部分被重新和重绘。重塑的泥塑十分粗糙，重绘的颜料也是对比非常强烈的大片红色、兰色、白色，完全破坏了早期彩绘的优美形象和艺术价值(彩图6XI, 6)。

彩绘所用的红色颜料主要是人面朱砂、朱砂与铅丹、或土红与铅丹的结合红色颜料。所用的白色颜料主要是石膏。
3. 彩塑的主要病害
3.1. 彩绘颜料的变色、褪色
由于莫高窟的彩塑，敷彩大量应用了红色颜料中的铅丹，特别隋唐时期，不论是彩塑还是壁画，铅丹是应用量最大、最普遍的红色颜料。由于铅丹在高湿度环境中，遇到碱性条件，是很容易变色的，由桔红色的Pb₃O₄变成棕黑色的PbO₂。经调查研究证明，新开挖的洞窟湿度很大，又由于碎岩中有许多碎石，岩面凹凸不平，以石膏为骨架的泥塑上面要敷很厚的泥层。木骨架的泥塑泥层也很厚。这样厚的泥层在通风不良的洞窟中不易干透，加上新开挖的洞窟本身湿度也很大。许多彩塑、壁画的质地又涂刷一层石灰，然后再进行彩绘。因此，彩绘上的铅丹是塑像完成不长的时间已经变色。彩绘应用的另一种红色颜料朱砂，长期受光照的影响，也已变暗。由于莫高窟的洞窟开凿在南北走向的崖面上，过去没有门，早晨太阳直射洞窟，这样的环境朱砂的变暗也很快。另外，由于莫高窟的彩绘颜料是矿物颜料，矿物颜料敷彩时必须掺加适量的植物胶或动物胶。这些有机胶结物，千百年来基本已老化失去胶结作用，使彩绘颜料层粉化掉落，颜料的密度大大降低，因而颜料彩度变淡，这就叫彩绘颜料的褪色。

3.2. 彩绘层龟裂起甲
由于彩绘颜料中加胶过量，或胶的浓度过大，使颜料层强度过低，导致膜壳、龟裂，甚至起甲剥离。
与壁画的起甲相比，莫高窟彩塑颜料层的起甲没有那么严重。

Fig. 1. The altar, left side, Funhuang, cave 205, a Bodhisattva, Tang Dynasty, its polychromy was changed. X-ray diffraction spectrum of the brown black pigment sample (from the right armpit of the Bodhisattva), mainly PbO₂.

图 1. 莫高窟第205窟佛台左侧，唐代变色菩萨塑像右腋下，棕黑色颜料试样的X衍射谱图，主要是PbO₂。

Fig. 2. Cave 334, Dunhuang, X-ray diffraction spectrum of the red pigment (from the lotus petal of the chief Buddha which in the Qing Dynasty was painted again), the main composition is Pb₃O₄·HgS.

图 2. 莫高窟第334窟，窟内被清代重绘主佛莲花瓣上红色颜料的的X衍射谱图，主要成分是Pb₃O₄·HgS.
3.3. 彩塑表面的泥层酥碱
莫高窟的彩塑虽然应用了河床或洪水沉积的粘土，但这种粘土中还有少量的可溶盐，主要是芒硝(Na₂SO₄)和石膏(βCaSO₄)。大型塑像的石胎岩体中，可溶盐的含量更高。当湿度急剧变化时，这些可溶盐面吸水量膨胀，又时常失水收缩。这样反复的膨胀使彩塑表面的泥层风化，严重者酥碱，使颜料层受到严重破坏。另外，莫高窟的岩体为松散、孔隙度极大的石岩，过去，部分上层洞窟顶壁薄，常有雨水渗漏。也有相当一部分下层洞窟被潮湿的沙子埋在里面，这些上层渗漏雨水和下层埋在潮湿沙子中的彩塑早已酥碱。

3.4. 彩塑泥层剥落肢体断裂及倾斜
以石胎为骨架的大型塑像，由于受水的作用所引起的可溶盐活动的影响，岩体风化，造成彩塑的泥层大块剥落。以木料做骨架的木制塑像，长期受潮湿环境的影响，捆扎在木骨架上的发芽草和芦苇草遭朽，而导致彩塑泥层剥落。

彩塑的肢体断裂，主要是由于石骨骨架接合处的激裂。塑像的倒下是由于由于塑像本身承重大，受地震等因素的影响，塑像的重心外移而造成的。另外，立像都是在地面上凿孔，将塑像的骨结构固定在地面上的岩体中，依靠的立像将塑像腰间的木骨骨固定在墙面上岩体中预埋的木楔上，当固定的木骨骨断裂或木骨骨质化而固定点松动，都会造成塑像倒下而遭受严重破坏。

4. 彩塑的修复保护
对于起甲、酥碱彩塑的修复，采用与起甲、酥碱壁画基本相同的修复材料和方法。由于莫高窟环境比较干燥，多年来采用聚醋酸乙烯乳液和聚乙烯醇修复壁画、彩塑起甲彩塑层，取得了很好的修复效果。其工艺方法是，将2-3%的聚醋酸乙烯乳液或2.5%聚乙烯醇1%聚醋酸乙烯乳液等1:4.1的混合胶结剂，用注射器注入颜料层下地仗层和起甲的颜料层。待起甲颜料层稍硬化具有一定柔韧性后，用丝绸包扎棉花做成的纱包将起甲颜料层微微按压，粘复在地仗上。近年来，我们对丙烯酸乳液和Paraloid-B-72修复起甲壁画、彩塑进行了实验。从观察短期效果还比较好，但最终效果有待进一步观察和鉴定。

目前，酥碱壁画、彩塑的修复还是一个难题。过去也用修复起甲壁画的材料修部分酥碱壁画，但过几年后，修复过的部位又开始酥碱，修复效果不佳。5年前，我们采用日本化学工业公司生产的7.5的硅酸铝(商品名称：(スノーテックス)在榆林窟进行过酥碱壁画的修复试验。从目前初步观察，这种材料对酥碱壁画修复效果较理想，但有待做进一步的深入研究。

对于泥层剥落的彩塑的修复，分两种类型进行。以石胎做骨架的大型彩塑，首先加固风化岩体。对莫高窟这种环境较干燥的风化砂岩石，以高模数的硅酸钾(即PS)加固风化岩体，其效果比较理想。待岩体加固好后，将剥离的泥层用稍加胶合剂的泥浆粘合复原。如果剥离的泥层体量较大，或在立面上承重较大，再用适当的锚杆锚固，当然锚杆要做的隐蔽，最后进行裂缝灌浆和修复。以木制骨架的小型彩塑，要更换遭朽的木骨架，或捆扎在木骨架上的发芽草和芦苇草，这就是进行脱胎换骨的修复。对倒下的塑像进行扶正、定位和重新加固固定。

对酥碱和颜料变色的防止，我们正通过环境监测和变化跟踪的研究，采用工程措施进行预防性保护，如对薄层洞窟的岩壁加固，岩体裂隙进行化学灌浆，以隔离雨水渗入洞窟内。对地下渗水的部位进行帷幕灌浆等工程措施，切断渗水。另外适度的通风，对防止壁画彩塑颜料层变色、酥碱也有较好的效果。

大量的游人进入洞窟，所排出的CO₂和水气也是引起壁画、彩塑地仗酥碱和颜料变色的因素之一。过去我们和美国GETTY保护研究会合作，做过这样的试验。40个人进入洞间为141m³的洞窟内37分钟，结果是洞窟中的CO₂比原来升高6倍，湿度和相对湿度也急剧升高，但CO₂排出却非常缓慢。可以想象，如果在一个中等大小的洞窟中，成天大量观众不断进入，窟内的CO₂和湿度就会累积升高，真是一个令人担忧的问题。虽然这个研究有必要进一步进行，但对中、小型洞窟的开放进行适当的控制，对防止壁画、彩塑地仗酥碱和颜料变色肯定会有好的效果。
Li Zuixiong

Coloured Clay Sculptures and their Protection at Mo Kao Grotto at Dunhuang

In the 492 caves of the Mo Kao Grotto at Dunhuang more than 2,500 clay sculptures, from Beiliang (4th century AD) to the Yuan Dynasty (14th century AD), covering 11 dynasties in all are kept.

The technology of making these coloured clay sculptures falls into two categories. The first kind of technology is for those medium-sized and small sculptures. One ties elders and reeds around the complete wooden framework to form man-like operations, whose height reaches 20-30 meters. Instead of wooden frames, stone bases are left when caves are dug. On the bases holes are cut to put in stakes on which rough and coarse grass clay is applied. The application of fine clay completes the sculptures.

All the clay sculptures of Mo Kao Grotto are coloured, but their colours vary from dynasty to dynasty. In the Sixteen States Period and the Northern Wei Dynasty, the colours were simple, ranging from earth red, mineral green, azurite, white to black. In the Sui and Tang Dynasties, the colours became bright and brilliant with many sculptures inlaid with gold. Especially at the zenith of Tang Dynasty, minium (Pb₃O₄) was used extensively. The skin colour of the sculptures became dark brown or dark coffee due to the big change of minium. In the Five Dynasties Period and the Song Dynasty the colours tended to be light and elegant. In the Qing Dynasty, the sculptures were remoulded and repainted with gypsum as the white pigment, ultramarine as the blue pigment and cinnabar as the red pigment.

Due to centuries of dampness, changes of temperature, rain-fall, rock percolation, the activity of soluble salt in the rock body and between rock layers, and other natural factors, the coloured sculptures have extensively suffered showing fading, colour change, cracking of the pigment layer, alkaline pulverisation, broken limbs and collapse caused by the decaying wooden frames, the dropping of clay caused by the weathering of stone bases, etc.

To protect and repair the sculptures we have taken measures such as setting up and reinforcing the collapsed figures, replacing or repairing the wooden frames, strengthening the weathered stone bases, repairing the pulverised pigment layers, thickening the cave roofs to prevent leakage and other environmental improvements. With the environmental monitor and analysis, we have control over the number of visitors in the caves so as to avoid the impact of CO₂ and moisture on the sculptures. See colour plate XVI.
故宫博物院的彩绘艺术品
——兼谈保护问题

故宫博物院收藏的带有彩绘的艺术品涉及范围相当广泛，主要有四大类：建筑装饰彩绘、壁画、彩绘和器物彩绘（在这里不包括书画、陶瓷彩绘、漆器制品和印染品等等），其中建筑装饰彩绘是故宫彩绘艺术品中数量最大、内容丰富、品种繁多、形式多样的一类。

中国古建筑主要是木结构，其建筑装饰彩绘是宫殿建筑的一大特色。有梁架上的彩绘及天花、藻井、屏门、隔扇、罩上的彩绘。主要是做在木构件、木板、墙体上的彩绘。也有在纸、布、绢上的彩绘。故宫建筑彩绘，不同的建筑，不同的时代，不同的功能，有不同的彩绘。在制作材料上也有区别，旋子彩画，也有点缀金之说。是古老的品种。现在能见到的元代还有，故宫神武门楼花板属于这一类（彩图XVII，1）。和玺彩画，以金箔为主，在明末清代就已广泛应用。主要用在后妃的宫殿和生活用房。例如三大殿等，内檐彩画采用真金做法。图案通体贴金与天花、藻井的龙凤彩画相呼应。同时也有大面积的环境气氛（彩图XVII，2、3、5、7）。宝珠吉祥类彩画风格粗犷、色调热烈，带有满族情的风格（彩图XVII，6）。也有带有典型的宗教色彩（彩图XVII，8）。在康熙以后，可能同康熙南巡有关，于宫廷彩画中吸取了江南比较自由的风格，主要用在后妃的生活和休息的地方。内容上出现了山水，花鸟，人物。戏文、西画（彩图XVIII，13、14）。

根据彩画需要，颜色也改变过去用单色的颜料的作法，为采用两种或两种以上的混合颜料。另外还有一种称之为海墁彩画或海墁天花，比较灵活，像带雕刻的彩画（彩图XVIII，9）。特别是倦勤斋，顾名思义，倦于勤政了，是乾隆皇帝为自己落位后用做休息的地方。室内装饰十分华丽雅致。其天花（彩图XVIII，10）描绘花卉，花朵饱满。枝叶茂盛与壁画所画园林景致映照呼应，栩栩如生。平添几分情趣，其中也反映出自觉不自觉的吸收了西方绘画的技法。在彩画颜料方面在清初雍正年间（约18世纪早期）已经逐渐引进了西方颜料，到十九世纪中晚期的同治年间，中国的建筑彩画已经大量采用洋青、佛青、洋红等西方颜料。

故宫博物院内壁画不多。有山西运山县兴化寺元代壁画——七佛说法图。为典型的寺庙建筑的宗教壁画。有长春宫的清代壁画，吸收了西方绘画透视学原理。在绘画风格及技法上都融合了西方绘画，是中西方文化交流的产物。院中另外还有不少的装饰性壁画。

故宫博物院收藏的彩塑，包括彩绘雕塑、彩绘泥塑。由汉魏、隋、唐、宋、元、明、清及至近代都有。同时还藏有彩绘木雕，彩绘石雕（图1、彩图XIX，16-21）。

器物彩绘，除了具有较高考古学价值的新石器时期的
彩陶和汉代彩绘（图2，彩图XIX，15）以外，每种古代工艺品、日用品、钟表机械、玩具、仪仗，都带有彩绘装饰艺术，品种繁多。

彩绘艺术品在各种文物材质中最为脆弱，较难保存，特别是在室内外部分，湿度、温度、光照、风、雨、虫、雷、火灾、环境污染……等等因素都能侵害彩绘彩画，造成龟裂、起翘、酸碱、剥落、褪色、变色……等等现象。历来都有采取保护措施，给予保护。

故宫博物院的彩绘艺术品，除了彩绘以外，作为主体的宫廷建筑群，在1911年辛亥革命以前，还是实用建筑。辛亥革命以后随着封建王朝的消灭，作为宫廷建筑群完成了它的历史使命。院内开始成为历史的遗迹、遗物，成为凝固的艺术品，把它作为文物来保护和保存。二十世纪的上半叶，对它的保护和修缮，基本上还是延续了传统的工程做法。在古建筑修缮过程中，对其彩绘艺术品采取原封不动、保持现状的做法，或者采用原材料、工艺，保持原来的风格进行修缮。近四十年来，随着文物保护意识的不断增加，特别制定了“不改变文物原状”的原则。随着科学技术的发展及社会工业化水平的提高对彩绘艺术品的保护技术有了很大的发展。

我们坚持“保护为主，抢救第一”的方针。文物一旦受损不可再生的历史遗存物，都具有一定的历史、艺术、科学价值，保留有历史信息。文物保护的原则，首先是保护文物本身的存在。更重要的是最大限度的保存它所固有的价值的科学性和完整性。任何一种对文物本身的技术处理方法，都应对文物本身不产生任何后遗症和对文物本身价值不产生任何的影响。所以在面临破坏的文物进行抢救，做必要的技术处理以外，对绝大多数文物来
The Polychrome Works in the Palace Museum and their Preservation

The polychrome art works in the Imperial Palace of Beijing cover a wide range of exhibits and fall into four categories: i.e., painting on architectural elements, wall paintings, polychrome sculptures and colouring on utensils. They do not include calligraphy, porcelain or lacquer ware or painted and dyed articles.

The examples of colouring on architectural elements are extensive, rich in content and great in variety; they include painted ceilings, sunken panels, screen doors and spear shields. They are to be found not only on construction elements, wood boards and walls but also on paper, silk and gauze and their pigments, coating, materials, technology and functions vary over the centuries.

The second category of wall paintings are few in number. They include a religious fresco of the Yuan Dynasty brought to Beijing from Xinghua Temple in Jishan County of Shanxi Province and a fresco of the Qing Dynasty, which is a product of the cultural exchange between China and the West. The last two categories are extensive, including coloured pottery of the New Stone Age and various art works of the Han, the Sui, the Tang, the Song, the Yuan, the Ming, the Qing as well as modern examples.

Polychrome art work is most fragile and most difficult to preserve, especially those pieces located outdoors. The traditional preservation technology is to repair or restore the works by using the same materials and techniques as were originally used. Today, in order to maintain the original look of the art objects, we try to use scientific methods: for example (1) controlling the environment to help protect the relics; (2) using a surface protection technique of polymer chemical materials on coloured surfaces; (3) using polymer chemical materials to reinforce the fresco in order to stop pulverisation and the falling off of the paint layers; (4) taking off frescoes by using adhesive gauze or using the traditional method of taking off calligraphic works of art and then transporting the damaged wall paintings to a safer place. See colour plates XVII-XIX.
Authors

Prof. Dr. HEINZ BERKE
Anorganisch-chemisches Institut der Universität Zürich
Winterthurerstr. 190, CH 8057 Zürich
E-mail: hberke@acit.unizh.ch

Dr. BIRGITT BORKOPP
Bayerisches Nationalmuseum München/ Bavarian National Museum Munich
Prinzregentenstr. 3, D 80538 München
E-mail: bay.nationalmuseum@extern.itrz-muenchen.de

Dr. VINZENZ BRINKMANN
Staatl. Antikensammlungen und Glyptothek
Meiserstr. 10, D 80333 München
E-mail: brinkmann@antiko-am-koenigsplatz.mwn.de

Prof. DERUN CHENG
Liberal Arts College, Northwest University
PRC 710069 Xi’an

Dr. SYLVIE COLINART
Centre de Recherche et de Restauration des musées de France
6, rue des Pyramides, F 75041 Paris Cedex 01
E-mail: sylvie.colinart@culture

Prof. ERWIN EMMERLING
Lehrstuhl für Restaurierung, Kunsttechnologie und Konservierungswissenschaft
Technische Universität München
Oettingenstr. 15, D 80538 München
E-mail: c.emmerling@rkki.arch.tu-muenchen.de

Prof. Dr. HANS VAN ESS
Institut für Ostasienkunde — Sinologie —
Ludwig-Maximilians-Universität München
Kaulbachstr. 51a, D 80539 München
E-mail: vanEss@ostasiien.fak12.uni-muenchen.de

Prof. HANYU GAO
China Textile University
Zhanwulu Road
PRC 200092 Shanghai

Dr. Egon Johannes GREIPL
Generalkonservator
Bayerisches Landesamt für Denkmalpflege
Hofgraben 4, D 80539 München
E-mail: poststelle@blfd.bayern.de

Direktor BAOFA GUO
Museum of the Terracotta Warriors and Horses of Qin Shi Huang
PRC 710600 Lintong, Xi’an
E-mail: bmybwy@iwh.com.cn

Dr. CHRISTOPH HERM
Schweizerisches Institut für Kunstwissenschaft/Swiss Institute for Art Research
Zollikerstrasse 32, CH 8032 Zurich
E-mail: Christoph.Herm@sikart.ch

Prof. CAIPIN JIANG
Central Academy of Fine Arts
PRC 100005 Beijing

Dr. ULRIKE KOCH-BRINKMANN
Staatl. Antikensammlungen und Glyptothek
Meiserstr. 10, D 80333 München

Dr. YINGLAN KIM
China Textile University
1882 Yuan’an Xiulu Road
Building for International Students
PRC 200051 Shanghai

Dr. DETLEF KNIPPING
Bayerisches Landesamt für Denkmalpflege
Hofgraben 4, D 80539 München
E-mail: Detlef.Knipping@blfd.bayern.de

Prof. RUIJIAN LI
Botanical Garden
Cuihua Nanlu Road
PRC 710061 Xi’an

Prof. Dr. ZUXIONG LI
Dunhuang Research Institute
PRC Gansu

Prof. Dr. CHUNMEI LIN
Tainan National College of the Arts
66 Ta-chi Village, Kuan-tien, 720 Tainan County, R.O.C. Taiwan
E-mail: linem@mail.tnea.edu.tw

Direktor SHOULIN LU
Science & Technology Department
Palace Museum
PRC 100000 Beijing

Dr. SANDRINE PAGÈS-CAMAGNA
Centre de Recherche et de Restauration des musées de France
6, rue des Pyramides, F 75041 Paris Cedex 01

Prof. SHU GUAN QIAO
Beijing Central Handicrafts and Fine Art Institute
6-3-602 Hongmiao Beili
Chaoyang District
PRC 100025 Beijing

Dr. PETRA RÖSCH
Kunsthistorisches Institut
Ruprecht-Karls-Universität, Ostasiatische Abteilung
Seminarstr. 4, D 89117 Heidelberg
E-mail: proesch@gw.sino.uni-heidelberg.de

Dr. INGO ROGER
e/o Lehrstuhl für Restaurierung, Kunsttechnologie und Konservierungswissenschaft
Technische Universität München
Oettingenstr. 15, D 80538 München
E-mail: rogner@rkk.arch.tu-muenchen.de

**Prof. Zongyan Shang**
Botanical Garden
Cuihua Nanlu Road
PRC 710061 Xi’an

**Dipl.-Restauratorin Cristina Thiem**
Lehrstuhl für Restaurierung, Kunstechnologie
und Konservierungswissenschaft
Technische Universität München
Oettingenstr. 15, D 80538 München
E-mail: thieme@rkk.arch.tu-muenchen.de

**Prof. Dr. Michael Petzet**
Präsident ICOMOS
Geschäftsstelle c/o Bayerisches Landesamt für Denkmalpflege
Hofgraben 4, D 80539 München
E-mail: michael.petzet@blfd.bayern.de

**Dr. Hans-Georg Wiedemann**
Trinkbachstr. 17
CH 8712 Stäfa bei Zürich
E-mail: wiedarchta@goldnet.ch

**Direktor Yongqi Wu**
Museum of the Terracotta Warriors and Horses of Qin Shi Huang
PRC 710600 Lintong, Xi’an

**Prof. Zhongyi Yuan**
Museum of the Terracotta Warriors and Horses of Qin Shi Huang
PRC 710600 Lintong, Xi’an

**Prof. Jizhu Zhang**
Botanical Garden
Cuihua Nanlu Road
PRC 710061 Xi’an

**Minister Tinhao Zhang**
Ministerium für Kulturgüterschutz der Provinz Shaanxi

**Prof. Zhijun Zhang**
Museum of the Terracotta Warriors and Horses of Qin Shi Huang
PRC 710600 Lintong, Xi’an

**Prof. Feng Zhao**
China Silk Museum
PRC Hangzhou

**Prof. Tie Zhou**
Museum of the Terracotta Warriors and Horses of Qin Shi Huang
PRC 710600 Lintong, Xi’an
作者

埃尔温・艾默林 (Erwin Emmerling)，教授，慕尼黑科技大学大学修复、艺术工艺和文物保护科学专业

海因茨・贝克尔 (Heinz Berke)，博士，教授，苏黎士大学无机化学学院

比尔吉特・博罗科普夫 (Birgitt Borkopp)，博士，慕尼黑巴伐利亚州国家博物馆

文岑茨・布林克曼 (Vinzenz Brinkmann)，博士，慕尼黑古希腊罗马艺术收藏及雕塑馆

钱德郁，教授，西安西北大学文学院（邮编：710069）

克里斯蒂娜・蒂米 (Cristina Thieme)，修复师，慕尼黑科技大学大学修复、艺术工艺和文物保护科学专业

汉斯・凡・埃斯 (Hans van Ess)，博士，教授，慕尼黑大学东亚及汉学学院

高永琪，教授，上海纺织大学（邮编：200092）

埃贡・约翰内斯・格莱佩尔 (Egon Johannes Greipl)，博士，教授，慕尼黑巴伐利亚州文物保护局

郭宝华，副研究员，陕西省历史博物馆（邮编：710600）

克里斯托夫・赫尔姆 (Christoph Herm)，博士，瑞士艺术科学研究所

蒋勇，教授，画家，中央美术学院（邮编：100005）

金.problemaic，上海纺织大学留学生楼

乌尔里克・科赫-布林克曼 (Ulrike Koch-Brinkmann)，博士，慕尼黑古希腊罗马艺术收藏及雕塑馆

西尔维・科利纳 (Sylvie Colinart)，博士，法国博物馆研究和修复中心

德特勒夫・克尼平 (Detlef Knipping)，博士，慕尼黑巴伐利亚州文物保护局

彼德拉・雷施 (Petra Rösch)，博士，海德堡大学艺术学院东亚部

李京辉，研究员，陕西科学院西安植物园（邮编：710061）

李京辉，博士，研究员，甘肃敦煌研究院

林立春，博士，副教授，台南艺术学院博物馆学研究所，台南县大崎村66号

陆寿麟，教授，北京故宫博物院（邮编：100000）

格罗纳 (Ingo Rogner)，博士，通讯处：慕尼黑科技大学大学修复、艺术工艺和文物保护科学专业

桑德尼・帕热斯-卡玛纳 (Sandrine Pagès-Camagna)，博士，法国博物馆研究和修复中心

米夏埃尔・佩策特 (Michael Petzet)，教授，国际古迹遗址协会主席，通讯处：慕尼黑巴伐利亚州文物保护局

乔万力，教授，北京中央工艺美术学院

尚宗燕，研究员，陕西省历史博物馆

汉斯-格奥尔格・维德曼 (Hans-Georg Wiedemann)，博士，瑞士米特勒-托德公司

吴永琪，陕西师范大学兵马俑博物馆

袁华，教授，陕西省历史博物馆

张继祖，教授，陕西省历史博物馆

张延喆，研究员，陕西省文物事业管理局

张志军，副研究员，陕西省历史博物馆

赵忠信，教授，杭州中国丝绸博物馆

周铁，副研究员，陕西历史博物馆

李明辉，研究员，陕西科学院西安植物园

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