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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, ochre 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 Tamoutnefret, 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, As_2S_3, 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 stele of Nytoua and Nytneb 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 (FeO·nH$_2$O).

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, $KFe_3(SO_4)_2(OH)_6$, identified by Le Fur in Middle Kingdom pigments in Karnak (Le Fur, 1994), and natrojarosite, $NaFe_3(SO_4)_2(OH)_6$. 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 Akhethetep 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 microscope analysis indicates that the composition of these sulphates is more complex than that of jarosite and natrojarosite. Their SEM-EDSX spectra show the presence of much sulphur and iron, associated with potassium in jarosite and with sodium in natrojarosite. Substitution of sodium by potassium gives rise to intermediary components. The proportion of these two alkaline elements can vary within a single mineral grain or layer of paint, as was found in the yellow used on the mastaba of Akhethetep. 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 whitish 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
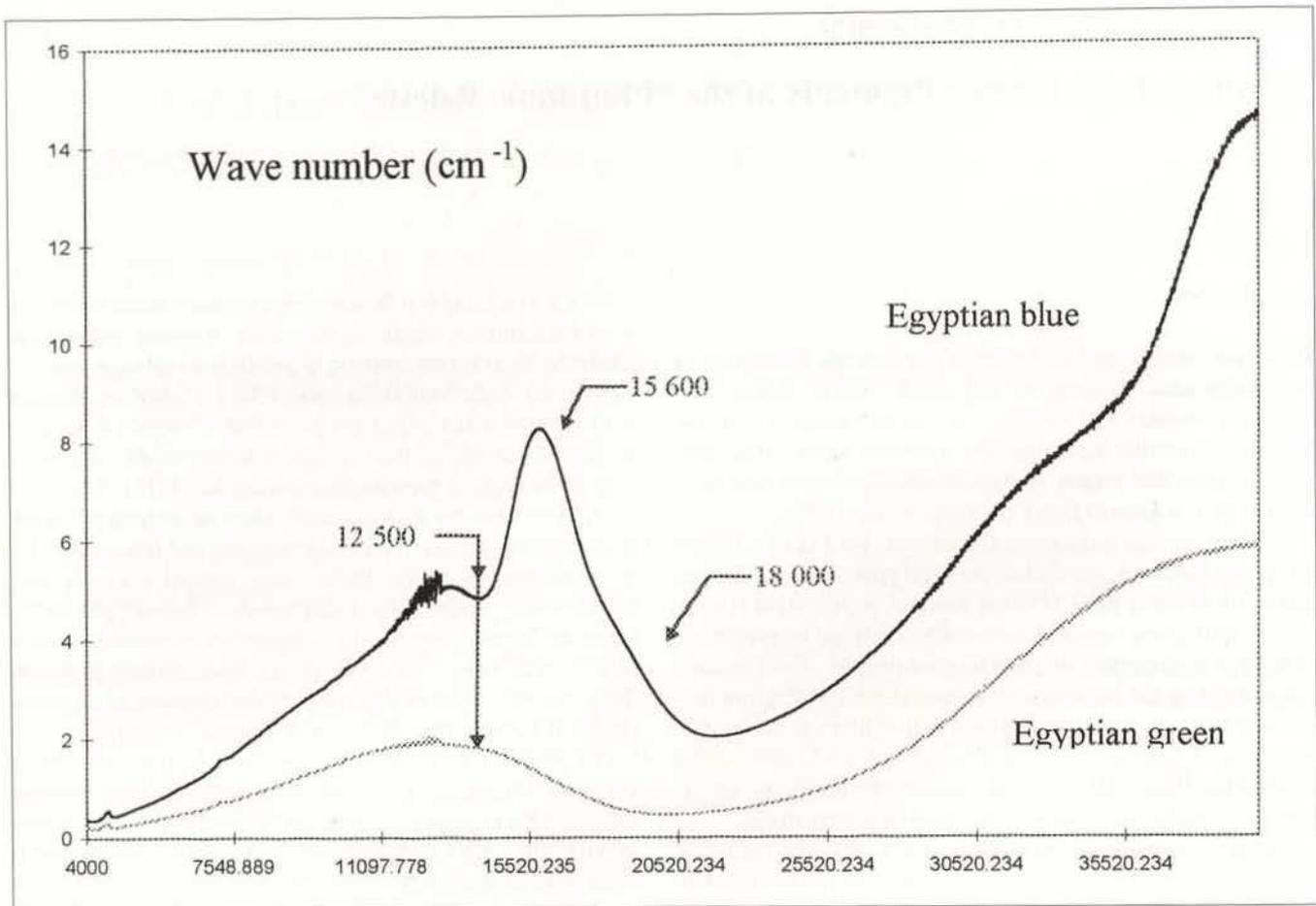
Fig. 1. Absorption spectra of the two calcium copper silicates. © LRMF, S. Pagès-Camagna.
图 1. 两种硅酸铜钙的吸收光谱。© LRMF, S. 帕热斯-卡玛纳。

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 Nefertiabet in the eponymous relief from Giza, for instance, is clearly meant to be made from panther's fur (4th dynasty, 2620–2500BC, 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-
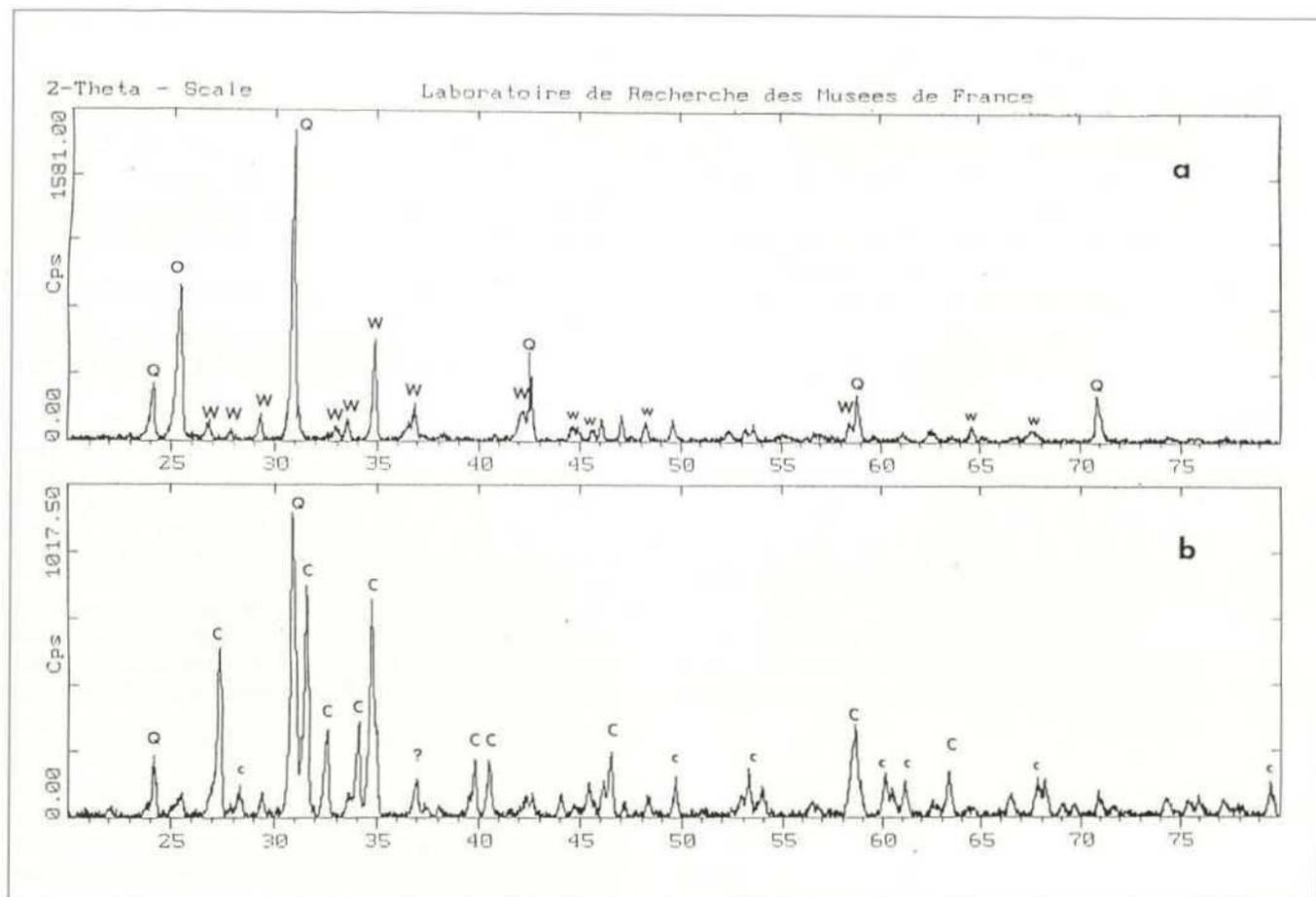
Fig. 2. X-ray diffraction of samples of Egyptian green (a) and Egyptian blue (b). W = parawollastonite, C = cuprorivaite, Q = quartz, T = tridymite. © LRMF, S. Pagès-Camagna.

图 2. 埃及绿(a)和埃及蓝(b)试样的 X 射线衍射。 W = 硅酸钙，C = 硅酸铜钙，Q = 石英，T = 鳞石英。© LRMF, S. 帕热斯-卡玛纳。

ted 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 DAE 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 LRMF 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 cuprorivaite ($CaCuSi_4O_{10}$), 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 Cu^{2+} in a square-plane environment in the crystalline cuprorivaite. It results from a mixture of compounds containing copper, calcium, silica and 1% flux around the cuprorivaite 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 parawollastonite ($CaSiO_3$) 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 Cu^{2+} 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. It is also notable 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 polychrome 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.

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科利纳 帕热斯-卡玛纳

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使用, 大型的纪念性作品和博物馆收藏的小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, 但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作不断的系统研究, 我们始终能获得新资料。法国博物馆的研究实验室(LRMF)对一些施彩的大型纪念性作品和人工制品(木棺、石刻浮雕和雕像)进行了研究, 这些实物保存在卢浮宫古埃及艺术部(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镜(SEM-EDXS)、拉曼显微镜和 X 光衍射。这些研究的目的在于确定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。

除传统的黄色材料如黄金、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: 即混有无水碱式硫酸铁的黄钾铁矾(科利纳, 1988 年)。这些矿物资在不同的石质制品和一些木棺上发现的, 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现为黄色层, 看来似覆有晶状物, 与其说是赭石和氧化铁色, 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, 是出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材料作为颜料: 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硅酸铜钙($CaCuSi_4O_{14}$)。另一方面, 还使用了一种过去所知和分析甚少的绿色合成颜料。它经常与埃及蓝弄错。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, 是变形阶段和结晶化与混合了 2 %黄铜的 b-硅灰石的混合物。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)