colorants

Review

The Modernity of Ancient Pigments: A Historical Approach

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Abstract: Naturally occurring and synthetic ancient pigments have a history of use spanning thousands of years. Curiously, some of their newly discovered properties make them excellent candidates for semiconductors, anticounterfeiting agents and so much more. In this paper, we will review their ancient roots in art and modern emergence as 21st century workhorses. You can never judge a pigment by its color alone!

Keywords: daguerreotyping; Egyptian blue; genetic engineering; indigo; Maya blue; medical diagnostics; Prussian blue; purple of Cassius; semiconductors; ultramarine

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1. Introduction

Pigments, first processed empirically and later by a developing technology in hearth or home, gave rise to some of the most remarkable works of art ever conceived. First discovered in the cave of Altamira (Spain) in 1878 [1] and dated to the Aurignacian period (35,000 to 23,000 before present, BP), the Stone Age artists' works testify to creativity, sensitivity and a capacity for abstract thinking that forever put to rest our modern image of lumbering brutes called "cave men." After viewing some of this cave art in Lascaux (France), Pablo Picasso (1881–1973) remarked, "They've invented everything" [2]; taking his cues from "them" as his teachers, he developed his signature talent of revealing the essence of things by stripping away the unnecessary details that encumber truthful perception. A striking example of this cave art—Picasso connection is the set of rhino drawings from the Chauvet cave shown in Figure 1. The depictions of chaos, violence, movement, strength and accompanying emotions seem to signal collusion between the artists involved, although the paintings are separated from each other in time by tens of thousands of years. Furthermore, the Chauvet cave paintings were first seen by modern humans in 1994, more than 20 years after Picasso's death [3].

This psychic link over eons of time is mirrored many times over in other more concrete connections in colorant and pigment usage that seem to bind the distant past to the present and point the way to the future. These relationships are the subject of the remainder of this paper, as outlined in Table 1. Each of these pigments has been selected as representative of a different type of material and covering a time span from antiquity to the present. In addition, within the past century, each has become valued for properties quite distinct from its color [4]. They will be discussed with respect to origin, history, chemistry and evolution into materials of great practical use in the modern world—uses, in some cases, never even dreamed of just a half-century ago.

Figure 1. A 20th century work of art is juxtaposed with Paleolithic cave art. (**a**) *Guernica* by Pablo Picasso (1937); (**b**) Rhino drawings from the Chauvet cave (France) dated to 32,000 to 30,000 BP.

Table 1. The ancient and historic pigments/colorants to be discussed in this paper.

Pigment/Colorant	Type	Date
Indigo	Plant-derived organic compound	Antiquity
Ultramarine blue	Naturally occurring mineral	~5000 BCE
Egyptian & Chinese blue	Synthetic pigment	~3200 BCE
Maya blue	Composite material	200–300 BCE
Purple of Cassius	Colloid	16th Century
Prussian blue	Synthetic pigment	1704–1707
Structural colors	Microlamellar array	1839

Before we discuss the individual materials in this paper, we should first set out some definitions of terms. Depending upon the method of application, all materials used for coloring other objects are categorized as either pigments or dyes. A typical dye must be dissolved in a medium, usually water, into which the article to be dyed is immersed. The dye becomes affixed to the article via a physical or chemical interaction. Colorants usually classified as dyes can also be used as pigments, but they cannot be applied directly to surfaces with ordinary binders, with a few exceptions, such as folium and orchil. Their inherent solubility causes them to bleed. Moreover, they have poor covering power and are largely transparent. To convert dyes into pigments, it is first necessary to render them insoluble. This is typically done by adding alum (potassium aluminum sulfate) to an aqueous solution of the dye and then adding an alkaline carbonate, such as potassium carbonate. In the resulting reaction, alumina (solid aluminum oxide) precipitates out of the solution and carries the dye with it. The resulting solid colorant is called a lake pigment [5]. Pigments, on the other hand, are insoluble solids that react only minimally with the substrate, although some inorganic pigments are known to do so under certain circumstances. They must be applied by first being suspended in a medium, called the vehicle or binder, which allows the pigment to adhere to the surface. The more general term colorant can be used to refer to both dyes and pigments.

2. Indigo: From a Coveted Blue Dye to Genetic Engineering

Indigo is arguably one of the most ancient coloring materials known to humanity. It is also one of the few naturally occurring colorants extensively used to this day. Blue jeans alone soak up most of the 70,000 metric tons produced each year. Because the people who lived along the Indus River in India were once thought to be among the first to dye with it, they got the naming rights, but perhaps unjustly. Its use has been definitively identified on textile samples from Huaca Prieta, Peru, that date to 6000 BP [6]. Its use on a robe in ancient Thebes has been dated to about 5000 BP [7], and on a mummy wrapping, dated to approximately 3580 BP [8]. It was described by Marco Polo (1254–1324), who encountered indigo on his travels, but its large-scale importation into Europe had to wait until the 16th century.

"Indigo" is actually the term for the mix of colorants extracted from about three dozen plant species that produce it. The major historically cultivated types were *Indigofera tinctoria* in India, *Isatis tinctoria* in Europe and *Indigofera suffruticosa* in the Americas. The chief component is indigotin ($C_{16}H_{10}N_2O_2$), the formal chemical name of which is 3H-indol-3-one, 2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro-, although the terms indigo and indigotin are synonymous in common parlance, denoting both the impure natural material and the purified chemical species.

Extracting the blue dye from the plant is both labor-intensive and difficult due to its rather complicated chemistry. It exists in the plant in the form of a precursor, indoxylic acid, a colorless glucoside. When the cellular structure of the plant is crushed in any way, such as by a feeding insect or a dye master, the plant's chemical defenses come into play to form presumably unappetizing indigo. Chemically, indoxylic acid's glucoside bond is ruptured enzymatically by ß-glucosidases also present in the indigo plant. These are only brought into contact with the indoxyl when the plant cells are broken open. Mashing and fermentation of the raw material in an alkaline solution (usually urine) for a few days was the ancient way to start the chain of chemical reactions; regular maceration (typically with bare feet) helped the process along [9,10]. Figure 2 shows indigo formation by (a) crushing the leaves and (b) the chemical sequence of events. Eventually, the desired deep blue indigo, insoluble in water, precipitated out and, when dried, could be cut into cakes for shipment or storage. Figure 3 is an archival photograph of workers in India cutting prepared indigo into cakes.

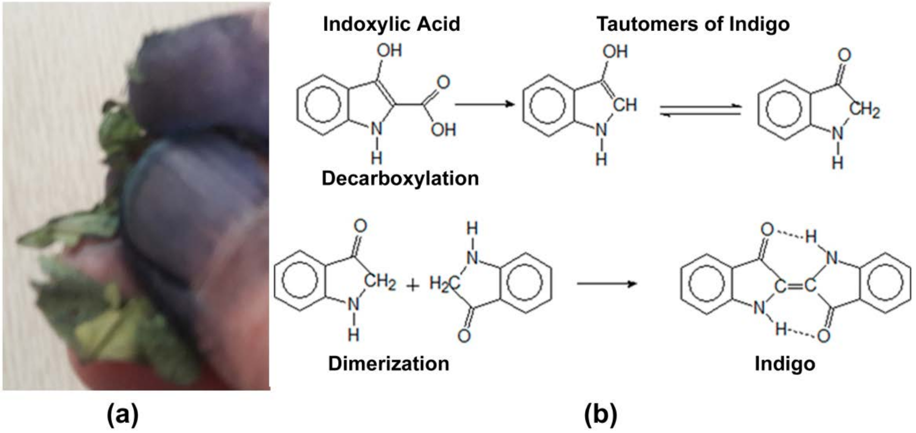

Figure 2. (**a**) Blue indigo formation from crushed *Indigofera* leaves; (**b**) formation of insoluble blue indigo from its indoxylic acid precursor.

Figure 3. Indigo workers in Allahabad, India, cutting the product into cakes (1877). Photograph: Oscar Mallitte. Public domain.

If, instead of a solid product, it is desired to directly dye textiles with indigo, then the fermentation bath should be maintained as an alkaline solution. When properly prepared, the broth should be near-colorless, indicating the presence of the soluble leuco form of indigo. After decanting off the plant solids, the materials to be dyed are soaked in the bath for a time and then hung out to air dry. The leuco form oxidizes spontaneously to insoluble blue indigo, which adheres to the textile fibers as tiny particles [11,12]. This process is completely reversible, the soluble, colorless leuco form being restored in the presence of a reducing agent, as shown in Figure 4.

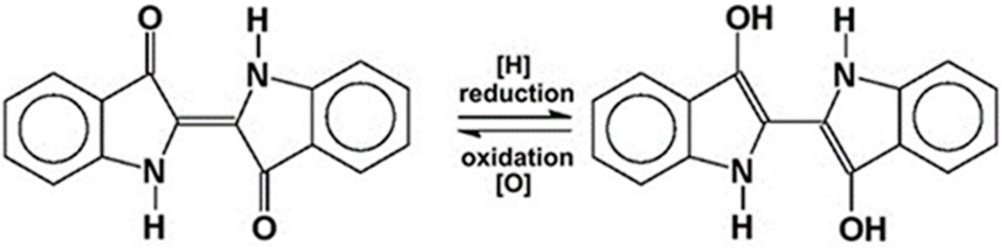

Figure 4. Reversible redox reaction of blue indigo (**left**) and its leuco form (**right**).

Because indigo was the most important industrial colorant throughout the 19th century, the great German chemist, Adolf von Baeyer (1835–1917), spent a great deal of time studying it. His aim was to determine the structure of the indigo molecule so as to develop a synthetic pathway that would do away with the wasteful and laborious processing of the natural product. Through step-by-step analysis of indigo's degradation products, he deduced that its fundamental building block was indole, C_8H_7N. However, it took him another 15 years to deduce the correct structural formula in 1883 [13]. Only after laboring for another seven years was von Baeyer able to develop a commercially viable synthesis protocol, mainly because the starting materials were so expensive. The breakthrough came in 1890 when another chemist, Karl Heumann (1851–1894), at the Swiss Federal Institute accidentally discovered how to produce a feasible starting material, anthranilic acid, from cheap and plentiful naphthalene. A broken thermometer spilled mercury into the reaction vessel, and the mercury reacted with the sulfuric acid therein to form mercury sulfate, which catalyzed the reaction. Figure 5 shows the reaction sequence of the first commercially feasible process based on anthranilic acid, which it took BASF (Badische Anilinen und Soda Fabrik, a German multinational chemical company) seven years to develop. Indigo went into production using this method in 1897.

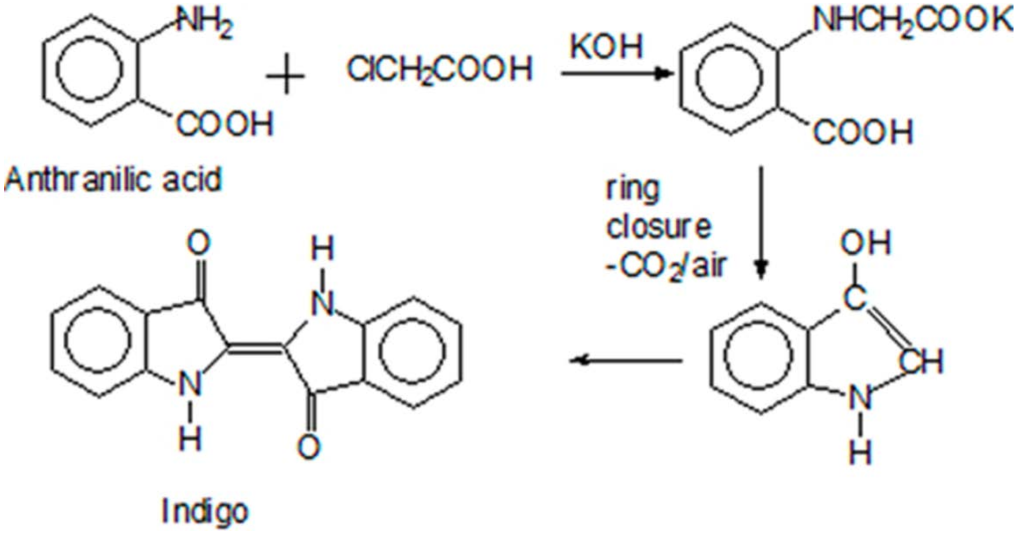

Figure 5. The 1897 synthetic pathway from anthranilic acid to indigo.

This single chemical reaction changed the world. It tolled the funeral knell of the natural products industry worldwide. The shockwave was first felt by the indigo plantations, especially those in India, where indigo was a single crop over a large part of the country. Within 17 years, from 1897 until 1914, the number of hectares of indigo planted in India diminished by an astonishing 83% [14]; worse yet, the drop in income was a crippling 93% [15].

World War I put an end to regular shipments of indigo. This situation forced industrially advanced countries, such as the United States, Britain and Switzerland, to develop their own synthetic indigo industries. By the end of the war, natural indigo had been relegated to a specialty material of interest only to diehard artists and historians. Furthermore, with today's regulatory requirements for sustainable synthesis methods, those that require large amounts of petroleum-based feedstock, such as aniline, cyanide, formaldehyde and corrosive redox reagents, are clearly untenable.

Two historical asides can speak to indigo's ease of synthesis and stability under stress. The first instance occurred in 1812, when Sir Henry Halford (1766–1844), physician extraordinaire to His Majesty King George III (1738–1820), reported the presence of a substance in the king's urine that formed an insoluble blue ring around the container near the surface. Almost 200 years later, 21st century chemistry Professor Wilfred Arnold investigated. The fact that the blue substance formed near the surface meant that oxygen was involved, he reasoned, and indole chemistry was clearly involved. Arnold's working hypothesis was as follows: enzymatic action on dietary tryptophan in the gut, abetted by putrefaction brought on by constipation, would lead to indole formation. If some of the indole was absorbed into the blood stream, it could be converted in the liver to indoxyl and then to the sulfate ester, i.e., indican. If the indican encountered a sulfatase, possibly from bacteria due to a urinary tract infection or contamination of the chamber pot, the indican would slowly hydrolyze to indoxyl, which, in the presence of air, would dimerize to insoluble blue indigo. Using this model, Arnold performed an experiment and found that the blue pigment did indeed develop after an incubation period of about two days and that the color was more intense if the pH was adjusted upward, which corresponds to the need for an alkaline dyebath [16]. Therefore, King George's body, under optimum circumstances, sponataneously synthesized indigo. Too bad that Adolf von Baeyer had to work 17 long years to accomplish the same thing.

The second story speaks to indigo's durability under certain stressful circumstances that also have to do with the digestive tract. Archaeological chemist Marvin Rowe was asked to date a Coptic textile that was contaminated by a mass of debris that turned out to be insect coprolites. Having no other food to munch on but the textile, the inevitable egestion of the waste material became embedded in the artifact. Rowe and his colleagues saw an opportunity to glean chronological data by analyzing the insect excrement, which was dark blue. They hand-picked about 3 mg of the fecal pellets and subjected them to plasma extraction preparatory to radiocarbon dating. The results revealed that the dark blue pellets were 1360 ± 70 years old. Although the moths were modern, the age of the carbon retained in the blue dye, more than likely indigo, remained unchanged during digestion. Durability indeed [17]!

Manufacturers of pigments and dyes, in an attempt to be more responsive to the growing concern over the tons of harmful pollutants entering the atmosphere and the world's waterways, are seeking to change direction and try natural, rather than petroleum-based, substitutes. Although for centuries, we have been exploiting mushrooms and lichens in textile dyeing, the verdict seems to have come down on microorganisms as the potential answer to the problem. A pioneer in this area is Natsai Chieza, who is using bacteria to dye fabric instead [18]. Genetically engineered bacteria programmed to produce a given colorant in a fermentation tank can be a game changer in the industry. A startup called Tinctorium has received a great deal of attention lately. Its cofounder and chief scientific officer, Tammy Hsu, is intent on producing greener blue jeans with genetically modified *Escherichia coli*. Her approach is to trick the bacterium into synthesizing indigo's water-soluble precursor directly in the dye bath. The eureka moment is when the indican is hydrolyzed right on the fabric to blue, insoluble indigo, thus avoiding the pollution engendered by conventional methods [19]. Talented biochemists can also utilize new gene-splicing techniques, such as CRISPR (clustered regularly interspaced short palindromic repeats), to program bacteria to produce any desired dye with the snip of a genetic scissor. A Korean team succeeded in synthesizing blue-pigmented actinorhodin from *Streptomyces coelicolor* with this method [20].

Once upon a time, the transistor radio was the hottest thing on the teenage circuit. Semiconductor technology allowed bulky vacuum tubes to be replaced with tiny silicon- or germanium-based chips, leading to easily portable electronic devices. However, no one ever dreamed that transistor circuitry might, in turn, give way to simple dyes and pigments that have been used for a very different purpose from ancient times.

The revolution began quietly enough in 1977, when the team of Hideki Shirakawa (b. 1936), Alan MacDiarmid (1927–2007) and Alan Heeger (b. 1936), working at the University of Pennsylvania, discovered that certain organic polymers could conduct electricity [21]. When their groundbreaking publication garnered the 2000 Nobel Prize in Chemistry, it spawned a tsunami-like wave of electronic innovations, such as organic light-emitting diodes (OLEDs), which are essential for smartphones and high-definition television.

However, it took at least another decade before the semiconducting properties of pigments received much attention. Because many of them are inexpensive, sustainable, biodegradable and biocompatible, they are ideal substitutes for traditional semiconductors. In particular, indigo, dibromoindigo (Tyrian purple) [22] and isoindigo (a geometric isomer of indigo) [23] derivatives have shown potential for applications in regenerative medicine, in the biomedical field as resorbable implants and for in vivo medical imaging. Additional applications inspired by natural indigo are in the areas of organic lasers, transistors, photovoltaics, photodetectors and photoacoustic applications [24]—truly an ancient colorant with a very modern twist!

3. Ultramarine: From Priceless Gemstone to Workhorse Blue

The land that lies beyond (ultra) the sea (marine) bestows its location on the name of its once most precious export, ultramarine blue, or lapis lazuli. From beyond the Caspian Sea, Afghans have wrested this shimmering gemstone from the intransigent bedrock of the Sar-e-Sang Mine for the past 7000 years. For millions of years before that, Mother Nature was slowly depositing this treasure in one of the most inaccessible corners of the earth, the High Pamirs of Afghanistan's Hindu Kush. The renowned international journalist Victoria Finlay put it this way: "After all, part of the mystery of lapis was that although for millennia it had travelled to Europe and Egypt it was always known to come from a mythical land so far away that . . . [e]ven Alexander had not managed to cast his greatly acquisitive eyes on the mines when he conquered the area 2300 years ago, and Marco Polo in 1271 had only nodded in its direction from another mountain range to the north [25]." Even Finlay had to try twice before she eventually reached the mine in 2001, the first woman in many a month, as Afghan women were forbidden to dwell there [25] (p. 307). Upon arrival, she ticked off the milestones of the whole of art history, from Egyptian tombs to Poussin's paintings, by analogizing the first 1000 feet of the mine as a timeline.

The raw mineral lazurite is the principal component of the rock, lapis lazuli, in combination with two other minerals, white calcite ($CaCO_3$) and white-gold pyrite (FeS_2). High-quality lapis lazuli contains smaller amounts of calcite and pyrite. The latter occurs as tiny, scattered grains and is responsible for the glitter in the gemstone. Because the blue material is intimately mixed with a high proportion of colorless silicates and aluminates, its extraction from these materials is a very laborious and time-consuming process [26].

Couple this processing with numerous price markups by middlemen, to say nothing of the transport costs from Afghanistan; all of these factors make ultramarine the most expensive colorant ever known, worth more than pure gold. Figure 6a shows an ingot of lazurite; the inset (b) shows the ground material to form a low-quality impure pigment.

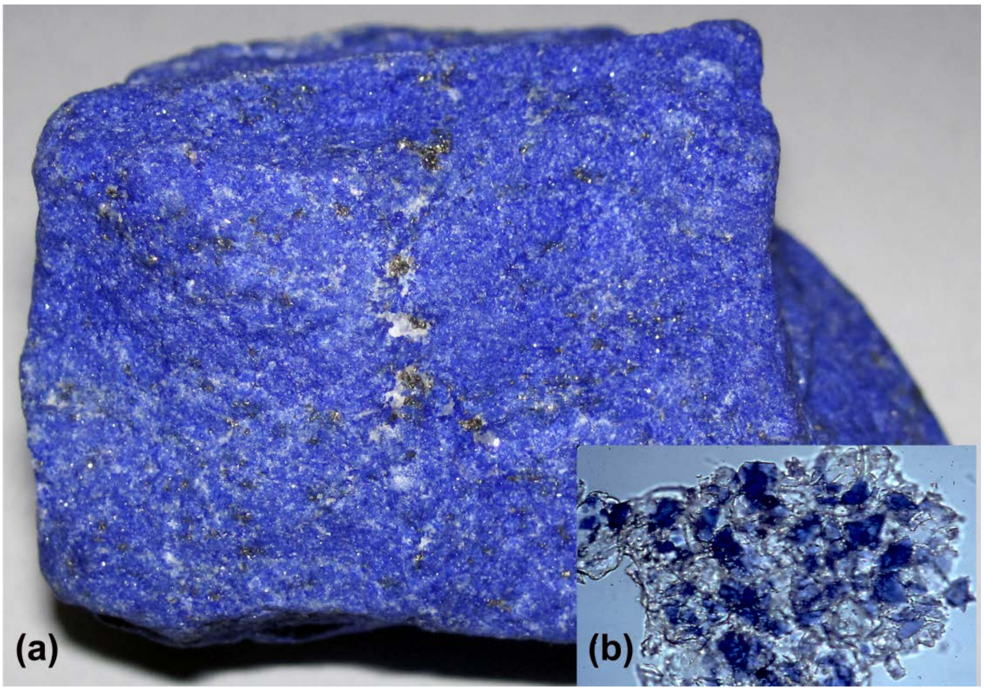

Figure 6. Ultramarine. (**a**) A fine example of lapis lazuli (lazuritic metamorphite) from the Sar-e-Sang deposit, Precambrian Sakhi Formation, 4.5 cm width; photo: James St. John. (**b**) Inset: natural ultramarine (photographed at 50× magnification). Note the large proportion of colorless material surrounding the blue portions; this indicates that the pigment was simply crushed lapis lazuli and that no attempt had been made to purify it further. Photo: Mary Virginia Orna.

Chemically, the pigment is an alumino-silicate clathrate, with the formula $((Na,Ca)_8(AlSiO_4)_6(S,Cl,SO_4,OH)_2)$, which encloses in isolated cages the unique chromophore responsible for the deep blue color, S_3^-, the trisulfide radical anion (Figure 7). The nature of this unit was the subject of speculation for centuries until F. Albert Cotton and colleagues finally solved the puzzle in 1976 [27]. They showed that a strong absorption band centered at around 625 nm was responsible for the blue color and that increasing the sulfur content appreciably deepened the blue. Because lapis lazuli rock was formed by contact metamorphism, the presence of sulfur in the pyrite may have contributed to the presence of sulfur in the clathrate. However, this arrangement is one of host crystal–guest ion, and replacing the guest ion with, for example, selenium, turns the pigment to a blood-red color. Furthermore, it is the trisulfide/disulfide radical anion, S_3^-/S_2^-, ratio that is key to the color, yielding blues to blue greens to greens to yellow greens to yellow as the disulfide concentration increases [28].

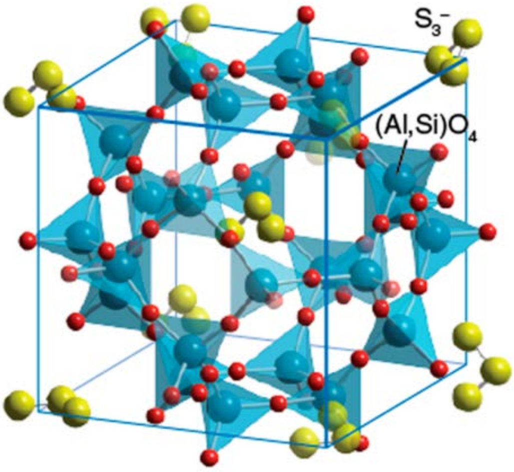

Figure 7. Ultramarine structure: trisulfide radical anions (shown as three yellow balls) in a host cage-like structure [29]. Color key: yellow–sulfur; red–oxygen; blue–silicon or aluminum.

Thanks to the superb analytical work of the great French chemist Nicolas Vauquelin (1763–1829), in 1814, the chemical composition of ultramarine and of a bright blue compound found in lime kilns was shown to be identical, although the series of analyses and attempted syntheses was far more complicated, stretching over decades from about the late 1780s to 1850. The biggest sticking point was the assignment of the chromophore, which almost everyone assumed had to be metallic. All the analysts who puzzled over the problem realized that the presence of sulfur was intimately involved; however, it was too much of a step to postulate that sulfur, in a unique configuration, just might be the chromophore [30]. Meanwhile, the French *Société d'Encouragement pour l'Industrie Nationale* decided to offer prize of FF (pre-1960 French francs) 6000 to the individual who devised a cost-effective route to the production of artificial ultramarine. A Frenchman, Jean-Baptiste Guimet (1795–1871), managed to produce and market an acceptable substitute for the real thing at a cost of about FF 850 per kilogram, which won him the prize, despite the fact that his price did not match the original requirement of FF 300 per kilogram. This is a far cry from 1541, when the price of natural ultramarine hit an all-time high, which amounted to about 55 times the daily wage paid to a skilled worker at the time [31]. Considering the price of the natural material, at FF 11,000/kg in Guimet's time, or USD 105.00/g at today's prices, Guimet's product was a bargain at USD 8.00/g, a price differential of 13:1 [32]. However, a German chemistry professor, Christian Gottlieb Gmelin (1792–1860), also claimed the prize for his independently and near-simultaneously developed method. As they were pursuing their priority dispute, other manufacturers got into the act, making every effort to keep their processes secret. By the end of the 19th century, almost three dozen firms were in the business, and the price differential between the natural and artificial product widened to eighty to one, quickly transforming a luxury blue into a mainstay commonplace colorant.

Today, the synthetic product can be produced for between USD 0.08 and 0.17 per gram [33]. Figure 8 is a graphic illustration of the exponential drop in synthetic ultramarine prices from the date of its introduction in 1826 until the last decade of the 19th century.

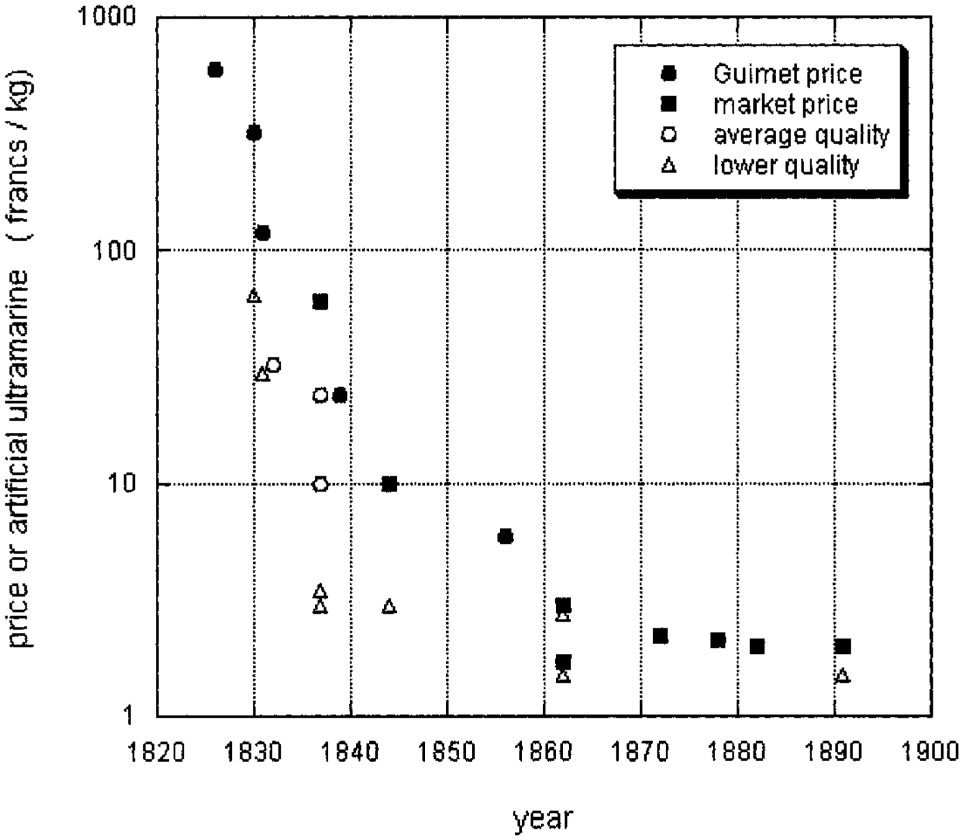

Figure 8. Evolution of artificial ultramarine prices. Black dots correspond to the best quality. Reproduced with permission from [33] (Figure 7.10).

Price was not the only factor that propelled ultramarine's metamorphosis from luxury item to workhorse pigment. It is one of the few brilliant pigments that does not contain a transition metal as the chromophore—a real ecological plus. In fact, it is so safe that it can be used with impunity in food containers, cosmetics, children's toys and any other applications in which the substance comes into contact with the skin or the mouth. It is also a superb pigment that can be used in virtually any kind of paint medium—oil, water, tempera, acrylic, alkyd, polyurethane and water-based emulsion coatings, with a single caveat: it decolorizes on contact with acid. It also finds many uses in inks, coatings, plastics and fibers [34]. Pete Cole, president of the paint manufacturer Gamblin Artists Colors in Portland, OR put it this way: "If you're trying to paint the colors of the natural world, there are colors you struggle with and there are colors that practically do it for you—ultramarine blue is one of those colors . . . It does its job so incredibly well [35]".

Aside from all these pedestrian applications, ultramarine ultimately rocks! Due to the prominence afforded by the high visual impact and global publicity of Yves Klein's (1928–1962) IKB (International Klein Blue), synthetic ultramarine has mounted the throne and displaced the iconic natural pigment with its own reality. (See Figure 9).

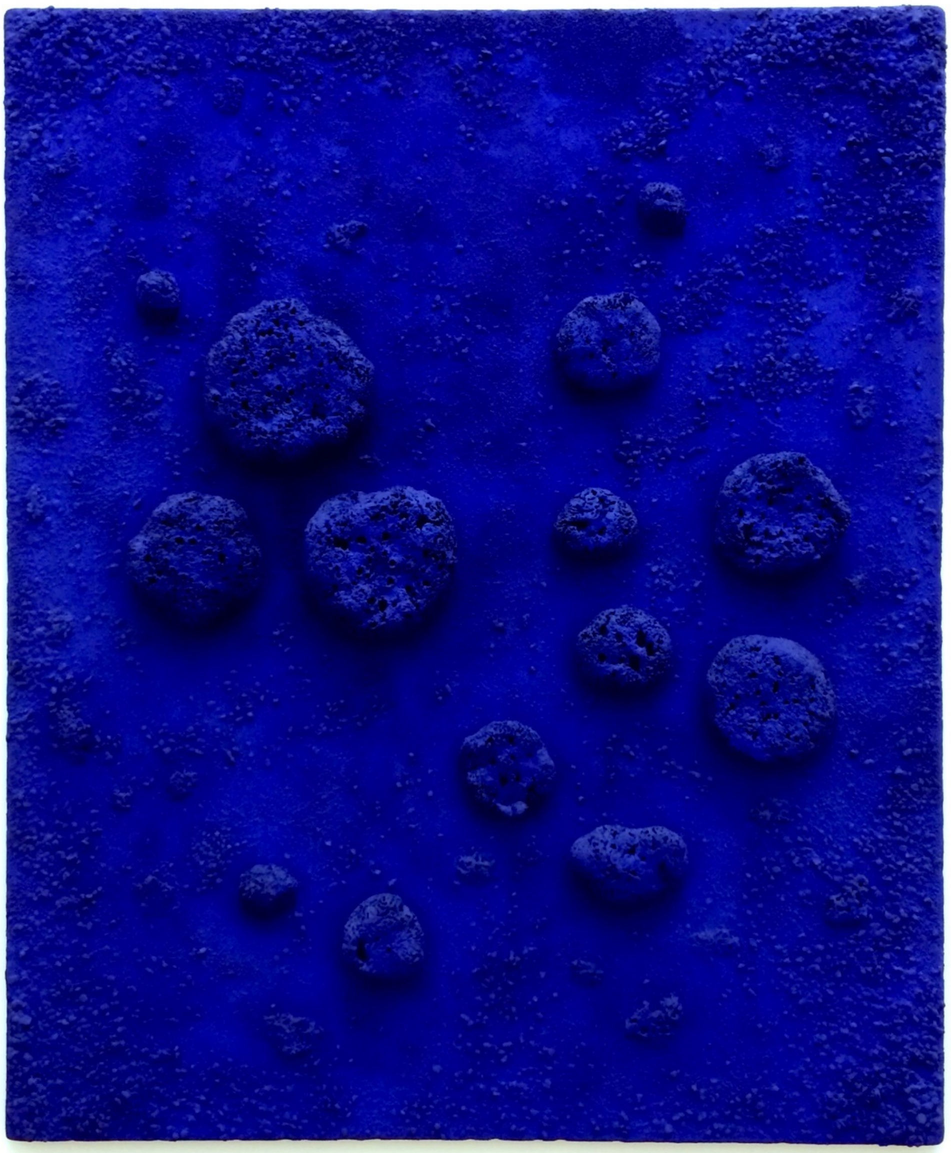

Figure 9. L'Accord Bleu. Mixed media painting, 1960. Yves Klein. Foundation Stedelijk Museum Amsterdam Collection [36].

The deep, luscious blue color has shaken off the captivity of form forever. Now immaterial, it has pervaded music, film, literature, academia, television and any other medium you might care to name to become the first postmodern pigment [37].

Unfortunately, synthetic ultramarine is also pervading the environment, as noxious air pollutants, such as SO_2 and H_2S, are needed for its formation. A Polish team has described a new approach whereby sulfur radical anions are encapsulated into zeolites, forming ultramarine-like pigments with a range of colors [38]. The jury is still out regarding the acceptability of these products into the ultramarine family.

4. Egyptian Blue: From Pharaohs' Tombs to Counterfeit Detection

Egyptian blue derives its label from the fact that its presence has been identified on Egyptian artifacts dating from the Old Kingdom, which flourished 4500 years before present, from 2575 to 2134 BCE [39], conferring upon it the distinction of being perhaps the first synthetic pigment in human history [40,41]. Because it is also the earliest example of the application of chemistry to investigation of the arts [42], by Johann Friedrich Gmelin in 1781 [43], it forms a bridge from the past to the present, from the ancient world of Ptah and

Osiris to the modern world of spectroscopy. Its detection in many other ancient world sites signifies its universal use, extraordinary stability and widespread availability. As nature was not very generous in providing naturally occurring blue pigments, it is possible that Egyptian blue was the only available (or affordable) blue pigment for millennia, other than the mineral azurite.

By way of analysis and experimental synthesis, we now know that the major ingredients in Egyptian blue manufacture are some form of copper, lime ($CaCO_3$), silica in the form of sand (SiO_2) and a flux, natron (a mixture of sodium salts, principally carbonate, bicarbonate, chloride and sulfate), likely collected by the ancient Egyptians from the Wadi al Natrun, from which the mixture takes its name. When these ingredients are heated to about 950 °C for a long period of time, preferably overnight (an astounding technological feat in ancient times, possibly accomplished by using a double bellows borrowed from iron works), Egyptian blue is formed [44]. Adolf Pabst determined the formula, $CaCuSi_4O_{10}$, by X-ray powder diffraction in 1959 [45,46]. Its naturally occurring counterpart is the relatively rare mineral cuprorivaite, which was discovered on the slopes of Mount Vesuvius in 1938 [47]. Mike Tite and colleagues have analyzed numerous samples of Egyptian blue from sites in Egypt, Rome and the Middle East. They found that some of the material, specifically from Nimrud and Nineveh, came closest to the stoichiometric composition (Figure 10), although some other localities are likely to contain many unreacted ingredients [48]. We know that the actual recipe for producing Egyptian blue was a closely guarded secret in ancient times because, despite the thousands of papyri found and examined, not one of them contains the recipe for its manufacture. It follows that the Egyptians treated the pigment as a precious export to other parts of the world from a few secure sites.

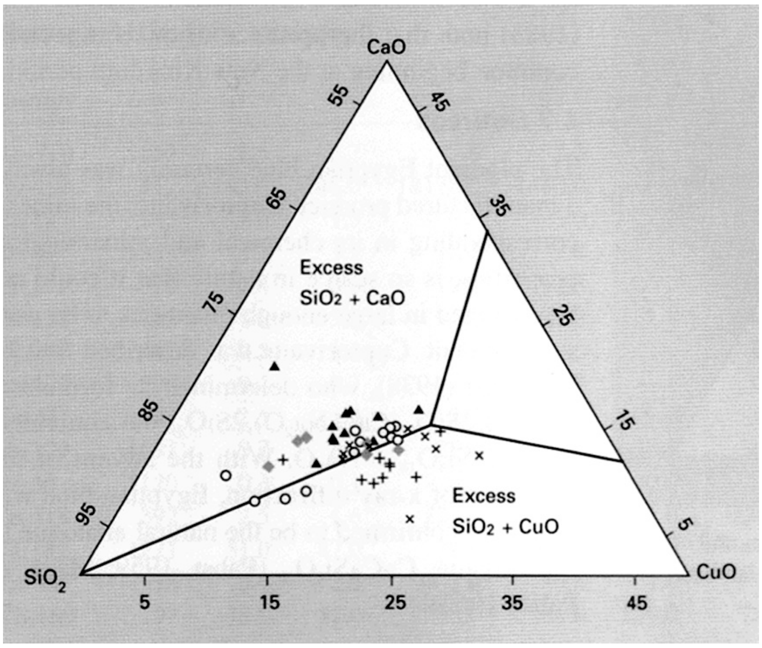

Figure 10. Ternary plot of silica, calcium oxide and copper oxide concentrations for Egyptian blue (normalized to 100%). The point at which the three internal lines intersect represents the stoichiometric composition of Egyptian blue. Sample Key: ○, Egypt; ▲, Amarna; +, Nimrud; ×, Nineveh; ♦, Rome (reprinted with permission from Ref. [48]; copyright 1984, American Chemical Society).

A similar pigment closely related to Egyptian blue is Chinese blue, or Han blue ($BaCuSi_4O_{10}$), the synthesis of which was independently discovered in the Far East. To form it, a barium compound was used instead of the calcium compound necessary to form Egyptian blue, as minerals containing barium, such as barium carbonate ($BaCO_3$) and barium sulfate ($BaSO_4$), were available. Because we know that the Chinese added lead compounds to the reaction mix, it has been proposed that this was an ingenious way of improving the yield of Han blue; lead has since been shown to act as a catalyst in this reaction [49,50]. Equations for the formation of Egyptian blue and Han blue are as follows:

$$\underset{\text{Malachite}}{Cu_2CO_3(OH)_2} + \underset{\text{sand}}{8SiO_2} + \underset{\text{lime}}{2CaCO_3} \xrightarrow{\text{flux, 800–900 °C}} \underset{\text{Egyptian blue}}{2CaCuSi_4O_{10}} + 3CO_2 + H_2O \quad (1)$$

$$\underset{\text{malachite}}{Cu_2CO_3(OH)_2} + \underset{\text{sand}}{8SiO_2} + \underset{\text{witherite}}{2BaCO_3} \xrightarrow{\text{Pb, 900–1000 °C}} \underset{\text{Han blue}}{2BaCuSi_4O_{10}} + 3CO_2 + H_2O \quad (2)$$

In both cases, we are witnessing a technological feat of mind-boggling proportions!

For both Egyptian blue and Han blue, the chromophore is CuO_4^{6-} in a square planar configuration. Embedding the chromophore in the tetrasilicate environment has a considerable effect on the d-d splitting, facilitating virtually complete absorption of the red, yellow and green regions of the visible spectrum, as shown in Figure 11 [51].

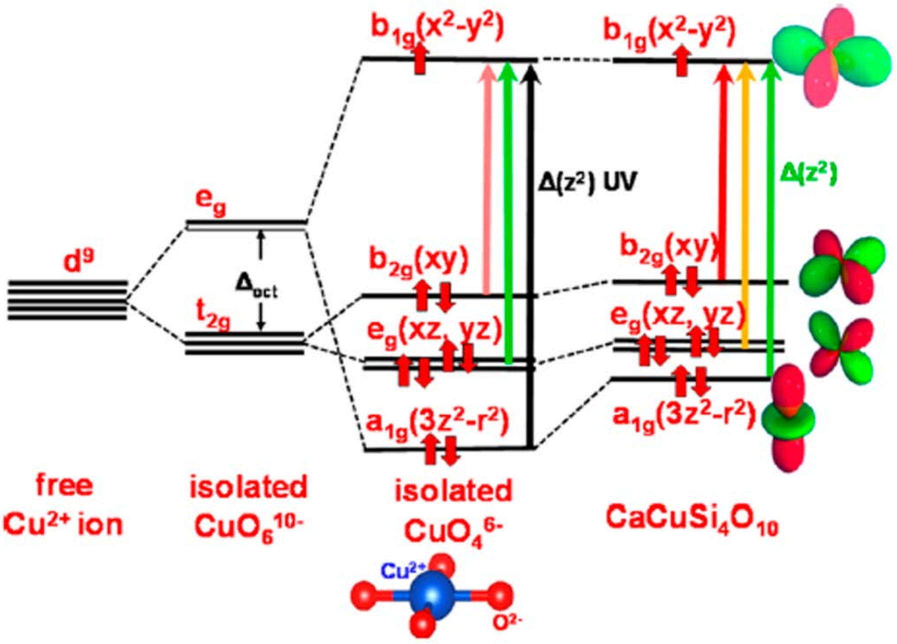

Figure 11. Qualitative diagram showing the splitting of d levels for Cu^{2+} in four different environments. Note the high energy elevation of the a_{1g} level from the isolated CuO_4^{6-} to that in $CaCuSi_4O_{10}$ on the right (reprinted with permission from Ref. [51]. Copyright 2016, American Chemical Society).

Excavations in Pompeii and Cumae demonstrate that the ancient craftsmen recognized the need for excess amounts of silica to produce the best Egyptian blue, although they could have no foreknowledge that a 21st century molecular orbital diagram would provide the theoretical basis for their protocol. One can even infer from the analyses that there was a quantitative recipe applied universally; however, aside from some procedural descriptions found on 17th century BCE Babylonian clay tablets, no written record of it existed [33] (pp. 21–22) until Roman author and engineer Vitruvius (d. 15 BCE) left us the recipe but curiously omitted limestone, a key ingredient [52]. Perhaps this omission led to the idea that the formula of Egyptian blue went missing in antiquity and that, therefore, its use died out in the early Middle Ages. Vitruvius was no help, but his recipe may have been useful after all if you were making the pigment in the right location. A major late Roman manufacturing center was Pozzuoli, on the slopes of Vesuvius. When workmen at that location mixed the requisite copper and silica to produce Egyptian blue, they would have inadvertently added the necessary lime because the sand in that area contains a great deal of it. If this factory was the major supplier of Egyptian blue, it would have had a limited availability throughout the Middle Ages. This explanation may account for its presence in a number of locations: illuminated manuscripts created in the 8th and 9th centuries [53]; 8th century wall paintings in the monastery of San Saba, Rome; 9th century works in the lower basilica of San Clemente, Rome; an 11th or 12th century *Last Judgment* in the Pinacoteca Vaticana; and a 13th century wall painting of the *Loggia dei Cavallieri* at Treviso [54]. A 2011 report pushed the late sighting of Egyptian blue well into the 16th century, when it was discovered in a 1524 Italian painting [55].

An even more exciting discovery of Egyptian blue's use during the Renaissance was its presence in Raphael Sanzio's (1483–1520) *Triumph of Galatea*, housed in the Villa Farnesina, Rome. (Figure 12). Italy's Accademia Nazionale dei Lincei, equivalent to the US National Academy of Sciences, scheduled a technical study of this fresco on the occasion of the 500th anniversary of Raphael's death. During their analysis using techniques such as visible reflectance, near infrared luminescence, macro X-ray fluorescence scanning, visible imaging and red induced luminescence, the scientists were astonished to discover Raphael's extensive use of Egyptian blue in the sky and the sea and even in Galatea's eyes in this fresco. Aside from the appearance of Egyptian blue as a pigment never in ordinary use in Renaissance painting, they certainly did not expect a new pigment to turn up on Raphael's palette, as his colorant usage had been so thoroughly studied through the centuries. This identification is the earliest instance of Egyptian blue's use in Renaissance painting; it is also the only known instance of its employment in all of Raphael's works [56].

Figure 12. Triumph of Galatea. Raphael (1513–1514), fresco; Villa Farnesina, Rome.

In scientific circles, Egyptian blue has received extensive attention with respect to both its nature and its manner of synthesis. Examining available samples of this elusive pigment, the first qualitative analysis of Egyptian blue, absent the decades earlier tentative work of Gmelin [43] was performed by the French chemist Jean-Antoine Chaptal (1756–1832) in 1809 on wall paintings excavated from Pompeii. The pigment must have been mixed with other substances, as Chaptal's list of components included alumina, along with the correct materials, silica, copper and lime [57]. Six years later, Humphry Davy (1778–1829) described what he found in lumps of a deep blue pigment from the baths of Titus in Rome: "sulphate of soda . . . .coloured with oxide of copper [58]". As sodium sulfate has never since been associated with Egyptian blue, Davy's report includes not only the pigment but its substrate or major impurity as well. In 1826, the renowned chemist Louis-Nicolas Vauquelin (1763–1829) identified copper as the source of the blue color in Egyptian blue but could not tell whether it had been manufactured by a wet or a dry process [59]. Analyzing the pigment quantitatively for the first time, he reported 70.2% SiO_2, 8.3% CaO, 16.4% CuO, 2.8% Na_2O and 2.3% mixed oxides of iron and aluminum [60]. According to our present knowledge, we realize that the sodium, iron and aluminum were impurities, which impeded Vauquelin from proposing a chemical formula. The most definitive piece of analysis came from the laboratory of the French mineralogist Ferdinand Fouqué (1828–1904) in 1889. Remarking that Egyptian blue ceased to be manufactured around the time of the barbarian invasions of Rome, he catalogued the numerous examinations of samples throughout the 19th century. Then, he gave his reason for his own work: "These numerous researches having been able to determine neither the exact knowledge of the chemical composition of the matter in question, nor a complete idea of its optical properties, and especially its reproduction having remained uncertain, I thought it necessary to resume studying it." Although he did not specify his source, his study must have involved a relatively pure sample of Egyptian blue [61] because he was able to produce, for the first time, the correct formula for the compound: "This blue (substance) is a double silicate of copper and lime having the formula CaO, CuO, $4SiO^2$, which can be deduced from analytical results" [62]. In modern notation, this formula is $CaCuSi_4O_{10}$.

Fouqué's work led directly to experimentation on the conditions under which Egyptian blue could be synthesized in quantities copious enough to satisfy, as he remarked, the needs of a nascent industry. A. P. Laurie and colleagues [63] reported a series of trials in which they found that the optimum temperature range for formation of the compound was between 850 and 860 °C held for 40 h and that, although not entirely necessary, successive grinding and mixing between heatings led to improved yields. They also expressed the necessity of adding a flux (sodium or potassium salts) to lower the melting point of the mix but emphasized that the blue formation does not depend on its presence. They took pains, however, to point out that "[t]he main point of interest . . . revealed by these experiments is the formation of a crystalline silicate under conditions which, the authors believe, have not been formerly recorded"—certainly a very low-key priority claim!

So, what is Egyptian blue's claim to modernity? The clue lies in the methods used to detect its unexpected presence in Raphael's *Triumph of Galatea*: near-infrared luminescence [56]. This is a singular characteristic of Egyptian blue and its close relative, Chinese blue or Han blue, that was not discovered until the first decade of this century.

It was first noticed by cultural heritage scientist Giovanni Verri when he began to investigate gleaming ancient white statuary and was struck by the fact that in their creases and corners, he could discern the tiniest traces of color. Intrigued, he probed further using a variety of instruments. He had observed what every museum scientist now knows was hidden in plain sight: that the ancient marbles, now seemingly white, were originally brightly colored polychrome pieces from which the fragile pigments had peeled off or been scrubbed off by over-zealous restorers [64]. Verri discovered that he could identify minute traces of Egyptian blue due to an unusual property; upon illumination with visible light, it luminesces intensely in the infrared region (700–1100 nm), but the effect must be recorded by an infrared-sensitive digital camera. When he digitally photographed the pigment, he reported that the recorded image gleamed like ice crystals [65]. Verri concluded by speculating on the exploitation of the luminescence properties of other cultural materials: "Further avenues of investigation include the measurement of the quantum yield, lifetime and absorption spectra of Egyptian blue, Han blue and Han purple and investigations of the behaviour of Egyptian green. The luminescence properties of other pigments, binders and other painting materials in the IR range are also under investigation".

This characteristic is a form of photoluminescence, light emission resulting from excited electronic states following absorption of electromagnetic radiation. The Irish physicist George Gabriel Stokes (1819–1903) first described it in 1852 [66] when he observed the blue glow of a quinine solution when ultraviolet radiation shone upon it. His studies resulted in the formulation of the law that bears his name, that is, the wavelengths of luminescent light were always longer than those of the incident light, although the mechanism involved would not be clarified until the advent of quantum chemistry, which provided the rationale for the spectral shift from the higher-energy incident light to the lower energy of the emitted light. The energy difference became known, appropriately, as the Stokes shift [67].

Figure 13 shows the reflectance spectrum of Egyptian blue. Beyond the limit of the visible region at 700 nm, there is some absorbance at 800 nm and then a large increase in reflectance that maxes out at 946 nm.

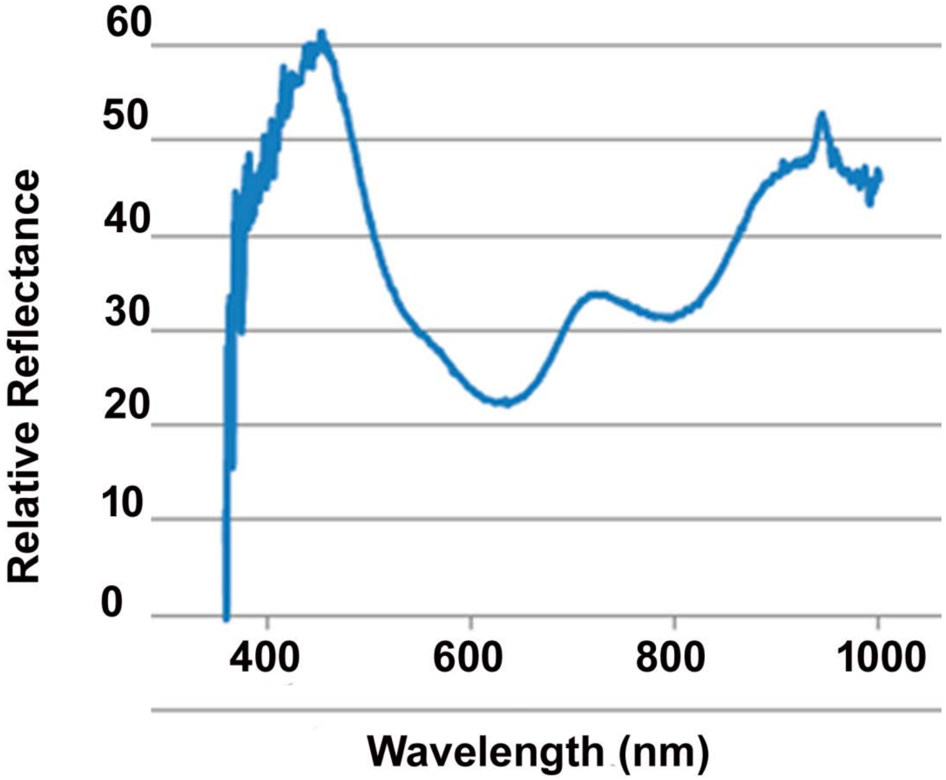

Figure 13. Reflectance spectrum of Egyptian blue powder.

Verri viewed this technique [68]—essentially visible-induced luminescence (VIL) digital photography—as a fresh, new, non-invasive technology for detecting materials that exhibit this behavior. He was able to demonstrate the presence of Egyptian blue on some well-known artifacts in the British Museum using this technique. Going farther afield, he also proved its presence on the wall paintings in the Tomb of Tutankhamen and in objects in the National Archaeological Museum in Athens, among other sites [69,70]. An exciting development reported in 2017 was the partial revisualization of wall paintings, largely invisible, in a Byzantine church (4th–7th centuries CE) now part of the Shivta UNESCO World Heritage Site in the Negev desert, Israel. Egyptian blue VIL photography pointed the way to mapping the distribution of Egyptian blue on an apse fresco of the Transfiguration, identifying areas and patterns that were not otherwise observable. Egyptian blue was detected throughout the painting as an underlayer that revealed a clear pattern, possibly as a sketch for the entire painting [71].

Although the optical properties of Egyptian blue have been examined and utilized over the past decade, scientists are now considering how to also probe the utility of its magnetic properties. Magnetic interactions of Cu^{2+} ions in cuprorivaite are being studied by electron paramagnetic resonance (EPR) and magnetic susceptibility measurements, raising the possibility of using portable EPR spectrometers to detect Egyptian blue and its degradation products in archaeological materials [72].

Ever since this unique characteristic of Egyptian blue was discovered, scientists have been speculating about other ways it can be used. One possibility is, given the appreciable transparency of human tissue to infrared radiation, that it could be used as a marker for new medical imaging techniques. It might also work as the basis for novel kinds of security ink to detect forgeries and counterfeiting. It could also serve as a fingerprint dusting powder on luminous surfaces, as it could be more easily seen [73,74].

There seems to be no end to potential innovative applications involving the luminescence properties of Egyptian blue, calcium copper silicate and its other alkaline earth metal congeners, strontium copper silicate and barium copper silicate. For example, a growing field in analytical chemistry, optical chemosensors, presents marked advantages over conventional analytical methods: low cost, non- or minimal invasiveness and lack of electromagnetic interference, to name a few. Working on the premise that Egyptian blue and other copper silicate luminescing materials combined with absorption-based indicators could result in robust multipurpose optical sensors, an Austrian-German team demonstrated their utility as simple, inexpensive inert references for ratiometric and dual-lifetime referencing readouts. Due to some unique features, such as broad excitation spectra in the green–red region of the visible spectrum, strong near-infrared emission with high quantum yield [75], long luminescence decay times, inertness to oxygen and high chemical and photochemical stability, they compare very favorably to other optical sensors currently in use. The team concluded that "the ancient pigments finally found a new life as components of high-performance sensing materials. Other potential applications of these exciting compounds in optical materials are yet to be discovered [76]".

Further work by a group at the University of Georgia demonstrated another significant property of Egyptian blue that may have additional implications for its conservation, as well as its modern usage. They discovered that when the pigment is stirred in a high-temperature (ca. 80 °C) water bath for several days, it forms a colloidal dispersion consisting of nanosheets (<10 nm thick) and nanoplatelets (>10 nm thick). Speculating about whether water-mediated delamination could take place in archaeological samples of Egyptian blue, they realized that the process would be very slow at lower temperatures but that the archaeological time scale is very long. Indeed, there are some examples in the literature [77] that show the presence of nanoplatelets in various degrees of detachment from the pigment surfaces. Therefore, not only is this discovery a warning signal to conservation scientists but also, perhaps, an avenue to a new class of two-dimensional nanomaterials, whereby an ancient pigment would enjoy applications through modern technochemical means [41].

Chinese or Han blue and purple, close relatives of Egyptian blue, synthesized, presumably, independently halfway around the world, both exhibit similar luminescence properties as the Egyptian variety. These two materials, synthesized with a starting material of witherite, $BaCO_3$, have the formulae of $BaCuSi_4O_{10}$ and $BaCuSi_2O_6$, respectively. Widely used during the Warring States Period (475–221 BCE) until the end of the Han Dynasty (206 BCE-220 CE), they were discovered by Elisabeth West FitzHugh on painted bronzes in 1983 [78] and, in subsequent work, in 1992 [79]. They have since been found on faience beads [80], on terracotta figurines [81] and wall paintings [82] and many other objects of cultural significance. A 2018 doctoral dissertation in material science described the hydrothermal [83,84] synthesis of Chinese blue as nanosheets that then rolled up spontaneously into what are called nanoscrolls [85]. The next phase of the work, according to the author, was to evaluate the structures for applications in the biomedical field.

Who knows what the future holds for these ancient inorganic pigments of immense cultural significance? This excursion into the history of one of the world's most unusual pigment families has been a journey full of surprises. For Egyptian blue, first, discovery; then, seeming disappearance in the Middle Ages; then, resurrection in discovery of its use in the Renaissance; then, entry into the modern world of chemistry through formulation and structural determination; and finally, celebrity status as a recognized addition to the industrial scene and the artist's palette, as well as a possible candidate for medical use due to its VIL in the near-infrared spectrum. For Chinese blue, there has been renewed interest in its history, its mode of synthesis, its relationship to Chinese purple, its heritage significance, its possible role in nanotechnology and applications for its powerful luminescence in the NIR. It is quite possible that the story is not over yet; modern chemical research being what it is, Egyptian and Han blues will surely figure in future studies of the characteristics of pigments and how they can be modified and utilized [86].

5. Maya Blue: From Indigenous Mystery to Nanotechnology

During the first decade of the 20th century, American archaeologist Edward Thompson (1857–1935) found that a natural geological sinkhole called the Sacred Cenote near the major Maya city of Chichen Itzá was a repository of many precious gold and jade artifacts. Realizing that these objects were possibly sacrifices intended to appease the gods, he continued to dredge deeper, uncovering a gruesome collection of 127 human skeletons embedded in a 3 m layer of blue sediment at the bottom of the well [87].

To the ancient Maya, blue was the color of sacrifice because it was the color of the rain god, Chaak. When the heavens above the usually arid Maya terrain stayed blue for too long, the only remedy was to send Chaak a sacrificial victim in exchange for a restorative rainfall. Because the desired water was blue, logic dictated that the color motif of the entire ritual should also be blue; painted entirely blue were the altar, the priests, the clothing, the victim and even the sacrificial knife [88].

Apparently, Thompson's original account of the sinkhole full of blue and bones went unnoticed by scholars and archaeologists until years later. It was not until 1931, when Herbert E. Merwin discovered the blue on a wall painting in the Temple of the Warriors in Chichen Itzá, Yucatán, Mexico, that this extraordinary pigment burst onto the international scene [89]. The hunt was on, and other wall paintings were soon uncovered. Among the most spectacular were those at the Chiapas site of Bonampak, the oldest accurately dated murals containing Maya blue [90] (Figure 14). Bonampak attracted immense interest because of the extraordinary durability of its fresco paintings; for about 1200 years, they survived exposure to a hot, humid climate without being completely degraded [91].

Figure 14. Temple of the Murals, Bonampak, Chiapas, Mexico. Ca. 580–800 CE. Photo: Arian Zwegers, 2013.

Provisionally dubbed by the misnomer Maya blue by Gettens and Stout [92], its use throughout Mexico and Central America was not limited to the territory of the Mayas alone. After many years of attempting to characterize the colorant [93], Gettens admitted to being completely baffled by this mystery. "This pigment", he wrote", not found anywhere else in the world, cannot be destroyed by boiling nitric acid, does not seem to be vegetable or organic in origin, is quite unlike any other known blue pigments—and we still do not know the true nature of the blue color principle. All we know is that the colorless inorganic base of the blue pigment is the clay mineral, attapulgite [now officially renamed palygorskite]; what makes the clay blue is still unknown". However, he added that G. W. Brindley's discovery in 1957 that the base clay material associated with Maya blue was the clay attapulgite (palygorskite) was the first great step forward [94].

Over the course of almost sixty years following Maya blue's discovery, scientists found that it was a technologically savvy yet easily made hybrid nanomaterial with an indigo chromophore intercalated as nanoparticles in a clay (magnesium aluminosilicate) matrix. One of its most astounding characteristics is its resistance to harsh chemical treatment, as well as its durability, even when subjected to degrading climatic conditions [95].

When Shepard and Gottlieb [96,97] performed their early X-ray analysis in 1962, they confirmed the previous work of Elisabeth West FitzHugh conducted earlier that year while she was working as an assistant to Gettens. She made the breakthrough discovery that the pigment was comprised of a clay, palygorskite, bound to an unknown chromophore [98]. West FitzHugh had also ventured to suggest that Maya blue might contain indigo somehow complexed with the clay, as no metal chromophore, such as the usual ones—iron, cobalt, or copper—could be identified [93]. Tae Young Lee, a member of the Gettens team, first identified the indigo pigment postulated by West FitzHugh [98]. The first and most important attempts to synthesize an indigo-palygorskite complex possessing both the color and stability of Maya blue was the work of H. van Olphen [99], which ranks with West FitzHugh's work as a high point in Maya blue research. In 1982, Littmann succeeded in making Maya blue from palygorskite and leaves from a Mexican indigo bush, pushing the reconstruction process along a little further [33] (p. 307) and [100]. It should be noted that van Olphen used indoxyl acetate, an indigo precursor, as his starting material.

The next great question revolved around the chemistry of how this complex formed; i.e., how does indigo, 3H-indol-3-one-2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2- dihydro), associate with the layered clay, palygorskite, with the general composition $Si_8(Mg_2Al_2)O_{20}(OH)_2(H_2O)_4 \cdot 4H_2O$? The palygorskite structure consists of a pile of layers of discontinuous octahedral sheets that produce structural tunnels with dimensions of 6.4×3.7 Å. These zeolite-like channels contain weakly bound zeolitic water, as well as tightly bound structural water coordinated to palygorskite's Mg^{2+} and Al^{3+} cations. As might be expected, the clay also harbors physisorbed water on its surface [101].

By molecular modeling, Giacomo Chiari and his group showed that the indigo was sterically compatible with palygorskite nanochannels, potentially being able to form strong hydrogen bonds between the structural water of the clay and the dye's carbonyl group [102]. However, they also showed that the adsorption enthalpies of water and indigo preclude the ability of indigo to displace the water in the clay body but, rather, can substitute for it once the water has been thermally expelled.

Sonia Ovarlez and colleagues provided the definitive solution in 2006 by heating mixtures of indigo and sepiolite at varying temperatures [103]. Below 130 °C, the indigo was simply surface-adsorbed on the clay, behaving like ordinary indigo. Heating between 130 and 300 °C was able to separate the indigo dimers and trimers from one another. The resultant indigo monomers were small enough to enter the sepiolite's ion channels, where indigo's nitrogen atoms could bond with sepiolite's magnesium ions to form a stable indigo/sepiolite complex. At higher temperatures (550 °C to 800 °C), the complex not only retained its structure but seemed to become even more stable.

The Ovarlez work, however, did not settle three important questions regarding (a) how the ancient Maya made the pigment in the first place, (b) the placement of the guest indigo molecules within the clay body and (c) why Maya blue found in various parts of Mesoamerica exhibits various hues, ranging from deep blue to a greenish tinge (Figure 15).

Figure 15. Detail from a page from the prehispanic Codex Cospi (aka Codex Bologna), Biblioteca Universitaria, Bologna, Italy. Typical Maya blue decoration that has retained its deep chromaticity, in contrast to the wall painting shown in Figure 14.

Regarding ancient synthesis protocols, there is no record, and anything we might learn will be based upon conjecture and experiments designed to reproduce a supposed original procedure. How the blue pigment indigo was married to a clay mineral could have been by accident, inadvertent rituals involving heating with copal resins or by a long tradition, the origins of which are lost in the mists of time. What we do know is that not any clay mineral would yield the stable blue material we now know; palygorskite's special properties are unique, and no other clay mineral would do [104].

In 1962, archaeologists discovered a white earth material, called *sak lu'um* by the local residents, in a cenote in the eponymous town of Sacalum in the northern Yucatán. Analysis revealed that *sak lu'um* was almost pure palygorskite, the host material for Maya blue. Present-day villagers continue to mine this unique substance for medical and art/craft/ceramics applications. Although several other palygorskite sites have been identified in Mesoamerica, it appears that Sacalum was the principal source in the pre-Hispanic era.

Numerous approaches to the second problem, i.e., how the indigo molecule is associated, indeed mineralized [105] with the clay body as an organic–inorganic hybrid, have been put forth but without conclusive proof or agreement among various groups working on this problem. Proposals on how the indigo is incorporated into the clay lattice center around how deeply or snugly the indigo is held in the clay body. A model proposed by Giustetto et al. [106] shown in Figure 16a has been found to be erroneous; thermogravimetric work by Chiari et al. indicates that the true picture is one in which the indigo molecules are more tenuously held nearer the clay surface [107,108], as shown in Figure 16b.

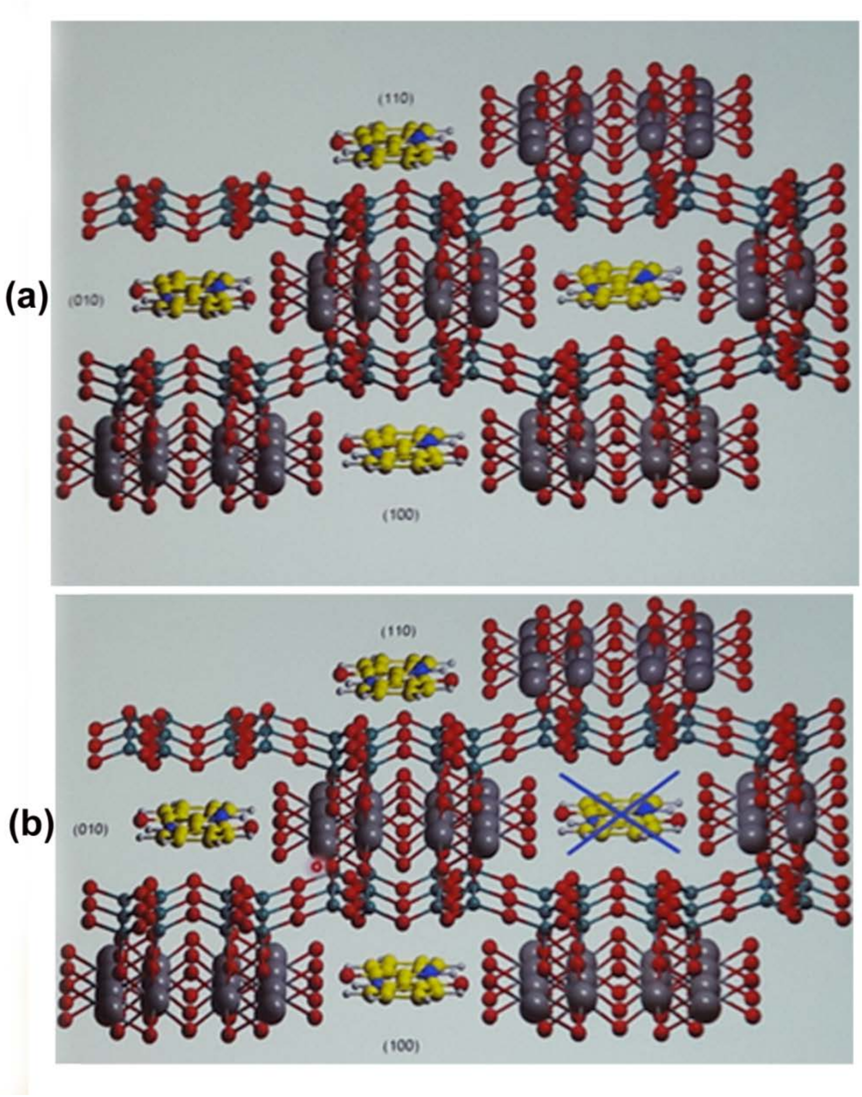

Figure 16. (**a**) Scheme showing incorporation of indigo molecules on the surface and internal palygorskite interstices. (Reprinted with permission from Reference [106]. Copyright 2005, American Chemical Society). (**b**) Corrected model showing that the occupation of internal interstices is not supported by experimental evidence.

Further work by the Giustetto group demonstrated that the nature of the host clay material affects Maya blue's stability. Clays with narrow ion channels allow the indigo to hydrogen bond to both sides of the channel, whereas channels with larger diameters can support bonding only to one side or the other, dramatically reducing host/guest interaction [109]. Additional work on Maya blue formation has led to the suggestion that an "all indigo" model of incorporation into the clay body is untenable. Vandenabeele and colleagues first reported the presence of leucoindigo based on Raman spectroscopic data [110]—unsurprising, as indigo (sometimes called keto indigo) can be transformed into several other molecular forms depending upon pH, the degree of thermal treatment and other processing methods. Figure 17 shows the structural formulae of several forms of indigo that can be formed by competing reactions.

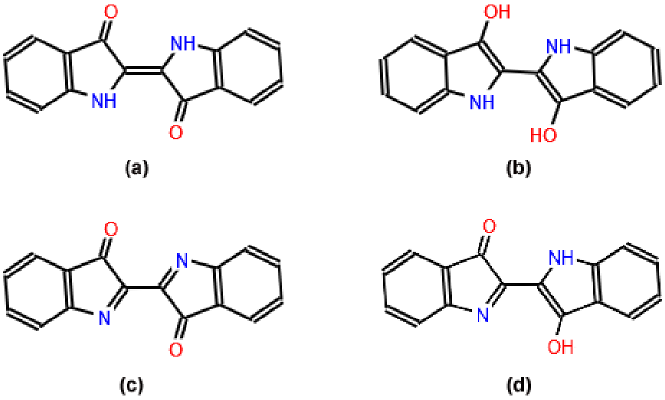

Figure 17. Structural formulae for (**a**) indigo (keto indigo); (**b**) leucoindigo; (**c**) dehydroindigo; and (**d**) indigo hemienol.

Ovarlez previously noted that keto indigo forms dimers and trimers that can be separated into the monomer by heat treatment, allowing the smaller molecule entry into the clay body more easily. However, indigo's near-planarity due to its central double bond would still impede its incorporation. Heat treatment of the mix in an alkaline medium could break that double bond to yield leucoindigo (b), which is both soluble in aqueous solution and geometrically more flexible. Once incorporated in the clay, contact with oxygen would restore the blue color of keto indigo. Solid-state optical and fluorescence spectroscopy have confirmed the presence of indigo's oxidized form, dehydroindigo (c), in archaeological samples of indigo, and because its spectrum is significantly red-shifted with respect to that of indigo, it would contribute to the variation in colors observed in Maya blue. It has been inferred that dehydroindigo's occurrence would also confer greater stability on the pigment because these molecules can penetrate more deeply into the clay support [111]. A novel proposal wherein indigo, upon mild heating, can isomerize to its hemienol (d), which, at elevated temperatures, could oxidize to dehydroindigo, would result in all three forms of indigo being present in the clay body. Such a mix could account for the observed variations in color in samples of Maya blue. Figure 18 is a schematic representation of this proposed mechanism.

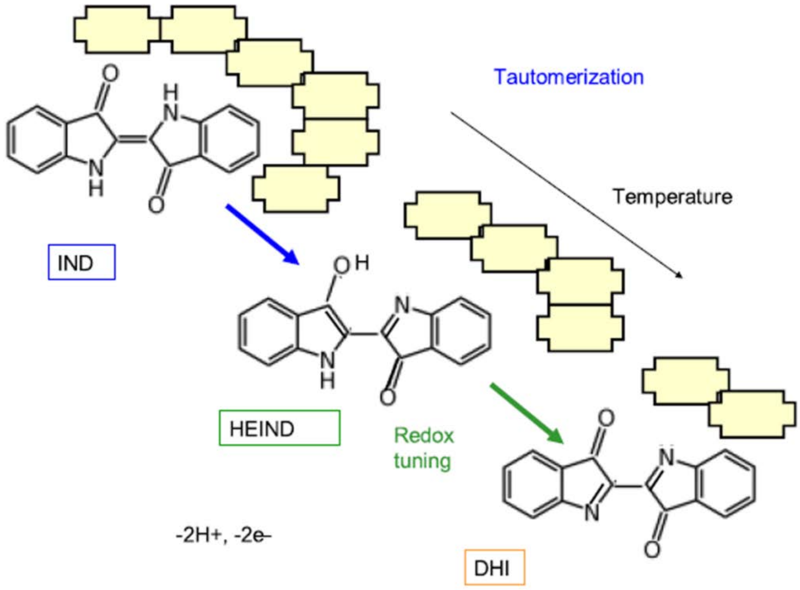

Figure 18. Schematic representation of the formation of Maya blue via tautomerization of indigo (IND) to indigo hemienol (HEIND) and redox tuning of HEIND to dehydroindigo (DHI). (Reprinted with permission from Reference [112]. Copyright 2021, American Chemical Society).

Evidence from UV-vis diffuse reflectance spectra, ATR-FTIR (attenuated total reflectance Fourier transform infrared spectroscopy) and solid-state electrochemistry supports the view that the characteristic greenish tint of Maya blue-type specimens is due to the formation of indigo hemienol and dehydroindigo [112].

Looking at the larger picture, it is quite possible to view Maya blue as a polyfunctional hybrid organic–inorganic material in which isomers and redox products of indigo, as major and minor components, are all distributed as guests in the host clay body. Furthermore, these components can participate in a variety of interactions with the host via hydrogen bonding, electrostatic attraction, van der Waals forces or direct ionic bonding, which, in turn, could modulate the physical properties and appearance of the colorant.

Various models for Maya blue formation including synthetic and analytical details were summarized in a literature review [113], resulting in the conclusion that (a) the ratio of dehydroindigo/indigo is directly proportional to the applied temperature and seems to figure as an important factor in controlling Maya blue's color and that (b) the degree of oxidation of indigo to dehydroindigo depends upon the nature of the clay support. The paper ends with the pronouncement: "The current study advocates the view of MB as a polyfunctional hybrid material whose properties are determined by the presence of different organic components forming different topological redox isomers in their attachment to the silicate framework."

Because Maya blue is considered a seminal example of hybrid organic–inorganic nanocomposites [101], a nanomaterial centuries ahead of its time, it will continue to fascinate each new generation for a long time to come. It will more than likely serve as an inspiration and model for the development of new hybrid materials [114]. It has certainly already inspired chemical educators to emulate our Mesoamerican forbears by having students synthesize it and its close relatives as an amazing topic to introduce students to scientific literacy [115,116].

Who knows where this interest and research will take us with respect to the development of new host/guest hybrid materials? One thing is certain: a combination of organic and inorganic components at the molecular level is a crucial aspect for the modern synthesis of hybrid organic–inorganic nanocomposites [117]. Furthermore, knowledge about how to control the inclusion, placement and configuration of organic molecules in the nanotube cavities of these nanocomposites is a critical challenge toward understanding their properties [118]. Viewed as a niche material within the broader category of nanomaterials made from clay minerals [119]. Maya blue has inspired the development of a family of similar materials with environmentally friendly preparation methods, assorted colors and excellent stability [120]. These nanocomposites have found use not only as pigments but also as photocatalysts [121] and photosensitizers [122]. The Native Americans of Mesoamerica hardly knew that their extraordinary discovery would be regarded as a springboard for novel kinds of materials and, at the same time, would both baffle and inspire those who came after.

6. Purple of Cassius: From Ancient Assyria to the Nobel Prize—And beyond!

Ancient physicians practicing alchemy paved the way to the isolation of alcohol through the arts of fermentation and distillation [123,124]. Alcohol's inevitable oxidation eventually led to vinegar, probably the first acidic substance ever isolated. As the centuries rolled on, alchemists learned how to make liquids similar to vinegar but far more powerful: the major mineral acids H_2SO_4, HCl and HNO_3 [125]. The latter two acids, hydrochloric and nitric, when combined, constitute aqua regia, i.e., royal water, a mixture capable of dissolving even recalcitrant gold to form a colloidal gold pigment sometimes referred to as Purple of Cassius. The earliest attribution of this substance is to the ancient Assyrians (2500–600 BCE), which presumes that they also knew how to make aqua regia [126], although no analytical information exists to back up this claim [127]. In fact, the Assyrian red glass found in Nimrud contained no gold at all but, rather, only Cu_2O and elemental dendritic copper, according to a 2009 study [128]. Therefore, we have to look elsewhere to establish the existence of aqua regia. A more realistic proposal for its source is most likely to be found in the work of the alchemist False Geber (ca. 1300 CE), De inventione veritatis (On the discovery of truth), published 2000 years later [129].

Once we have aqua regia in hand, we can look further for its use in dissolving gold to form Purple of Cassius. As early as 1597, German physician, alchemist and professor at the University of Jena Andreas Libavius (ca. 1550–1616) made note of the beautiful red color obtained from gold dissolved in aqua regia. In 1660, Johann Glauber (1604–1670), best known for the compound that bears his name, sodium sulfate or Glauber's salt, discovered an effective and economic way of manufacturing the red color. Although Glauber himself never profited from his find, another distinguished chemist of the time, Johann Kunckel (1630–1703), exploited its potential by producing sizeable quantities of it at the Potsdam Glass Factory. Many samples of Kunckel's work survive to this day (see Figure 19). However, Andreas Cassius the Elder (1605–1673) of Leyden seems to get all the credit due to a posthumous publication arranged by his son in 1685, some dozen years after his father's death [130].

Figure 19. Gold ruby glass. Schatzkammer Wittelsbacher, München Residenz. The piece on the right is attributed to Johann Kunckel.

Regardless of what it was called, it was the nature of Purple of Cassius that mystified chemists for centuries. Jeremias Benjamin Richter (1762–1807), whose great claim to fame is the law of definite proportions, scornfully wrote in 1797 that it was only a mixture of tin calx (tin oxide) with finely divided gold [131]. In 1806, Joseph Louis Proust (1754–1826), the discoverer of the law of constant composition, raised it to the level of a true compound without specifying how metallic gold and tin oxide were actually combined [132]. In 1857, Michael Faraday (1791–1867) continued in this vein by hypothesizing that Purple of Cassius was essentially finely divided gold associated with more or less oxide of tin [133].

He began by looking at gold deposits formed by deflagrating gold wire with the explosions of a Leyden jar and observed that "[w]hen any of these deposits of divided gold are heated to dull redness, a remarkable change occurs. The portions which before were violet, blue, or green by transmitted light, now change to a ruby, still preserving their metallic reflecting power, and this ruby is in character quite like that which is presented in "the arts by glass tinged by gold [133]". This description is uncannily reminiscent of the 4th century CE Roman Lycurgus cup, appearing ruby red in transmitted light but green in reflected light. There is speculation that the Roman glazier added a gold–silver alloy to the glass melt, unaware that gold was the critical component. In any event, production of ruby gold was very restricted and does not appear to have outlasted the fourth century [134].

However, Faraday was not content to simply observe with the naked eye. He continued: "The state of division of these particles must be extreme; they have not as yet been seen by any power of the microscope. Whether those that are ruby have their colour dependent upon a particular degree of division, or generally upon their being under a certain size, or whether it is consequent in part upon some other condition of the particles, is doubtful; for judging of their magnitude by the time occupied in their descent through the fluid, it would appear that violet and blue fluids occur giving violet deposits, which still consist of particles so small as to require a time equally long with the ruby particles for their deposition, and indeed in some specimens to remain undeposited in any time which has yet occurred since their formation. These deposits, when they occur, look like clear solutions in the fluid, even under the highest power of the microscope [133]". Later experimentation on Faraday's original gold colloids showed that the gold particles in his preparations had an average size in the 6 ± 2 nm range [135,136], leading many scientists to take exception to the claim that Richard Zsigmondy's (1865–1929) 1912 experiments with an immersion ultramicroscope heralded the birth of nanotechnology [137].

Faraday was arguably touching upon a phenomenon that, taken up by the Viennese chemist Richard Zsigmondy in the early part of the 20th century, demonstrated conclusively that these "ruby particles" of Faraday were comprised of very finely divided gold with colloidal stannic acid ($H_2SnO_3 \cdot H_2O$). Zsigmondy further demonstrated that a mixture of colloidal substances could behave like a chemical compound [138]. His work was in response to a difference of opinion among some outstanding chemists. For example, J. J. Berzelius (1779–1848) considered that this mysterious substance was a true chemical compound, whereas others thought that it was merely a mixture of finely divided gold and stannic acid. Zsigmondy's goal was to determine which of these views was correct. Furthermore, some scientists suggested that it was a true solution; others supposed that it was a suspension, despite the fact that it did not behave like a normal suspension and settle out. However, its nature as a true solution could not be verified by osmotic pressure experiments.

Various factors came together to crystallize Richard Zsigmondy's focus on Purple of Cassius. During his formal education, he was encouraged by one of his mentors, Rudolf Benedikt (1852–1896), to pursue his lifelong interest in the colors of substances, which he concretized by performing systematic studies on the luster, color and chemical composition of Bohemian glass. His earliest publications were in this field [139,140], but most significantly, he dedicated two years of his postdoctoral research with August A. E. E. Kundt (1839–1894) to the colors of colloidal gold in organic suspensions prior to firing on porcelain.

In his Nobel Laureate lecture, Zsigmondy said that he, "was dealing with gold orpiment glass and with certain ceramic dyes which were based in principle on extremely fine gold divisions. It seemed to me particularly remarkable that the effect of very closely allied chemical compounds could be fundamentally different in regard to the preparation and appearance of these dyes. This observation seemed to me all the stranger as compounds with completely opposite properties frequently produce similar effects on the dyes of extremely finely divided (i.e., colloidal) gold. These results could not be brought into harmony with the previous experience of chemistry. Consequently, I sought to discover the reason for these phenomena in a way other than the purely chemical one. The first special object of such investigations was the *Purple of Cassius*" [141].

The deeper he delved, the more Zsigmondy understood that this substance lay somewhere between solutions and suspensions in the unreconnoitered territory called the colloidal state. To investigate its nature, he realized that he would have to try to directly observe, measure and count solute particles, and for this, he needed to devise new instrumentation. Breaking new ground on two fronts, Zsigmondy invented what we now call the ultramicroscope—both slit (with Henry Seidentopf (1872–1940)) and immersion types—and with these instruments, he found that he could actually calculate the average mass and size of individual colloidal particles. (Figure 20).

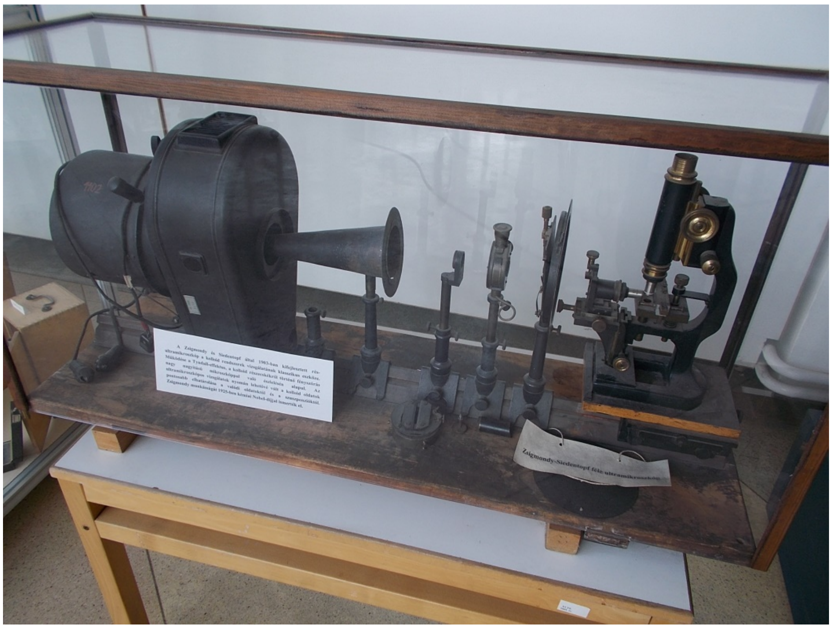

Figure 20. The 1902 slit ultramicroscope of Richard Zsigmondy and Henry Siedentopf. Eötvös Loránd University, Faculty of Science, Budapest.

In their breakthrough 1902 experiment, Siedentopf and Zsigmondy's sample consisted of very finely divided metallic gold uniformly diffused through a piece of glass. Using a complicated system of condensers, they were able to focus a very small but intense beam of light on the glass from the side. This arrangement allowed the individual particles of gold to be observed from above as distinct luminous points. By knowing the amount of gold in the glass and then by counting the number of particles in a definite volume observed through their microscope, they were able to calculate the size of the particles. They found that they could see particles as small as 0.005 microns, reducing the previous limits of visibility by forty-fold [142,143]. Siedentopf later went on to apply the method to observing ultramicroscopic bacteria [144].

An unintended benefit of this approach was the fact that Zsigmondy could demonstrate the reality of molecules and the fundamental discontinuity of matter. This was a hotly debated issue at the turn of the 20th century. Despite theoretical and inferential support for the existence of atoms, prestigious holdouts, such as Ernst Mach (1838–1916) and Nobel laureate Wilhelm Ostwald (1853–1932), refused to be convinced [145].

Over the following several years, numerous other scientists, such as Albert Einstein (1879–1955) and Jean Perrin (1870–1942), used the ultramicroscopic technique to obtain the experimental data that finally convinced skeptical physical chemists that molecules were real [146,147]. The great Wilhelm Ostwald finally conceded the point in 1906.

Zsigmondy's direct observation of solute particles marked a turning point in chemistry on other fronts as well. His methodology launched the new discipline we now call molecular biology by making it possible to study proteins and other biological macromolecules. For this classic work, Zsigmondy received the Nobel Prize in Chemistry in 1925 [148].

Aside from its role in providing experimental evidence for the particulate nature of matter, Purple of Cassius, aka colloidal gold, has been recognized since at least the Middle Ages for its remarkable medicinal properties. In the first book ever published on the preparation, uses and results of colloidal gold ("essence of gold") treatment, the author, one Francis Anthony, physician of London, documents case after case of successful treatments of such diseases and difficulties as high fevers, intestinal obstructions, complicated childbirths, paralysis and even epilepsy [149]. Flash forward to the 21st century: we now find colloidal gold, in the form of nanoparticles and nanostructures, at the forefront of medical applications due to their biocompatibility, specificity, optical properties and the ability to precisely control their physicochemical parameters. These properties make them ideal for imaging, diagnostics, therapy and drug delivery [150,151]. More specifically, colloidal gold immunochromatography has been used to detect severe fever [152], gold nanoclusters have been found to be most suitable for targeted gastric cancer therapy [153] and gold nanocages show great promise as optical imaging contrast agents [154]. Colloidal gold can also play an important role in monitoring banned substances in foods [155] and biosensing applications [156].

Nanoparticulate gold also displays extraordinary catalytic properties with respect to selectivity and oxidative activity due to gold-substrate, e.g., Au–O and Au–CO, bond strength variability with co-ordination number [157].

7. Prussian Blue: From Alchemical Accident to Semiconductor Technology

Imagine yourself in early 18th century Berlin. In 1704 or thereabouts, we are visiting the laboratory shared by Johann Konrad Dippel (1673–1734), a shifty alchemist, and Johann Jacob Diesbach (ca. 1670–1748), an inept color maker. Their workplace may have resembled something like Figure 21; however, given their penchant for accidents, it was probably a lot more shambolic.

Figure 21. An Alchemist in his Laboratory. Oil painting by a follower of David Teniers the Younger (1619–1690). Wellcome Library, London. Public Domain.

A setting like this is an accident waiting to happen—and happen it did. Diesbach routinely manufactured his signature red pigment called "Florence Lake", although its relationship to Florence was tenuous at best. Messily mixing its key ingredients, cochineal dyestuff, alum and English vitriol (iron(II) sulfate), he ran out of the alkali necessary to form the hydrated alumina that would precipitate out the dye [158]. Dippel, his lab mate, came up with some waste potash, and due to the slovenly nature of the setting, the potash was impure; it was contaminated with a fair dose of animal oil from distilled blood. When Diesbach combined the two mixtures, he witnessed a surprising alchemical miracle; the blend metamorphosed into a glorious, deep blue. Both men immediately realized that they had a potential fortune bubbling away in the pot.

Diesbach, staying put in Berlin, immediately formed a startup "Berlin blue" business, keeping his process top-secret for two entire decades. Meanwhile, Dippel made off for the Netherlands, where he marketed the product as "Prussian blue" for about ten years [159].

John Woodward (1665–1728), an English naturalist, revealed Diesbach's process in 1724 by publishing the recipe in Latin, claiming to have received it in a personal communication from Germany [160,161]. Harley summarized the recipe as follows: "To an alkali calcined with bullock's blood, dissolved and brought to boiling point, a solution of alum and ferrous sulfate was added while also boiling. During the effervescence which followed, the mixture turned green, and, after it had been allowed to stand, it was strained. The residual greenish precipitate turned blue as soon as spirit of salt (HCl) was poured on it [162]". Given the animal ingredient, she classified it as an organic pigment.

The mysterious nature of the chemistry behind Prussian blue's synthesis persisted for more than two centuries. Before Prussian blue came on the scene, pigments could always be classified as either organic or inorganic, but this new blue pigment uniquely sat astride the two categories. Carl Wilhelm Scheele (1742–1786), in Germany, described a strange-smelling gas he produced by heating it. Joseph Louis Gay-Lussac (1778–1850) later identified Scheele's material as the highly toxic gas hydrogen cyanide (HCN). Because HCN is lethal within 10 min at 27 ppm, it is fortunate that neither chemist sniffed the gas for very long. Subsequent analyses showed that the pigment contained potassium, iron and cyanide in the ratio of $KFe_2(CN)_6$, allowing us to deduce by hindsight that the necessary ingredients were the ferrous ion provided by the English vitriol and cyanide ion arising, in some way, from the organic material. The essential but then-unknown ingredient cyanide was probably produced from molecules containing the C–N bond, such as hemoglobin [163].

As Prussian blue gradually became a highly coveted pigment, 18th and 19th century chemists had their hands full trying various methods to improve the quality and quantity of this elusive material. No one as yet understood its chemistry, which conferred on it a certain aura of witchcraft. Eventually, chemists empirically discovered that they needed no alum or animal material to make Prussian blue; atmospheric nitrogen or ammonia could supply the requisite nitrogen, thus placing the pigment squarely in the inorganic camp. The origin of the intense blue color was found to be due to the presence of both Fe^{2+} and Fe^{3+} in the same molecule. Mixed-valence compounds absorb electromagnetic radiation by the charge-transfer mechanism and, in the case of Prussian blue, by absorbing almost all of the wavelengths of visible light except those in the blue region [164].

Prussian blue was an instant success among artists and colorists, who immediately incorporated it into their palettes. Within just a few decades of its discovery, it had become the blue pigment of choice for oil painting. It was present in the paint box of Jean-Honoré Fragonard (1732–1806) in two different formulations; other noted artists, such as Thomas Gainsborough (1727–1788), Vincent Van Gogh (1853–1890) and Pablo Picasso (1881–1973) also began to use it [165] (Figure 22).

Figure 22. Vincent van Gogh: Starry Night, oil on canvas, 1889. Museum of Modern Art, New York, NY. This celebrated, iconic painting is awash with Prussian blue pigment.

However, its durability depended upon the medium and circumstances of application. For example, George Field, in his 1885 treatise, *Chromatography* [166], condemned it as a "vacillating pigment" that "has the singular property of fluctuating under certain conditions, according to whether the surroundings are favourable for it to acquire or relinquish oxygen." He said it also darkens in damp and polluted air, such as that found in his test compartment, a shut-up privy. It is also fugitive in fresco; the pigment rapidly decomposes in alkaline medium to form brown hydrated ferric oxide [167]. However, the actual structure and chemical composition were not determined until 1977 [167,168]. Accepted formulae are $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$, bearing the chemical name iron(III) hexacyanoferrate(II), $KFe[Fe(CN)_6]$ and $NH_4Fe[Fe(CN)_6]$.

It was not long before Prussian blue became a workhorse pigment in household items and laundry bluing. Throughout almost all of the 20th century, it was the most commonly used blue pigment, ceding first place status to phthalocyanine blue only in 1970 [33] (pp. 147–161). Because it is also photosensitive, a property discovered by chemist and astronomer Sir John Herschel (1792–1871), it is the blue pigment in blueprints that changed the way architecture was done. Victoria Finlay [25] (p. 313) describes this property as follows: " … Prussian blue became the basis of something that changed the face of architecture and design forever: the first ever industrial photocopying process … . in 1842, [Herschel] realized that if he held a pattern drawn on tracing paper over photo-sensitive paper and shone a lamp over both of them, the bits that were not protected by dark lines would change their chemical formula in the light. They would shift subtly from ammonium ferric citrate to ammonium ferrous citrate". The photosensitive material is essentially the Fe(III) (ferric) ion, which, upon exposure to ultraviolet light from the sun or from some other source, is photoreduced to a Fe(II) (ferrous) ion. Once the paper has been activated, it can then be sprayed with or immersed in a solution of potassium ferricyanide, which then reacts to form Prussian blue:

$$\mathrm{Fe}^{2+} + \mathrm{K_3Fe(CN)_6} \rightarrow \mathrm{KFe[Fe(CN)_6]} + 2\mathrm{K}^{+} \tag{3}$$

This is a two-step process that Finlay describes, but it is also possible to combine both the ammonium ferric citrate and the potassium ferricyanide, impregnate a paper with the mixture and carry out the exposure in a single step. The paper, in either case, should then be rinsed to remove unreacted ammonium ferric citrate. Finlay continues: "The resulting ghostly pattern of white lines on blue paper was called a 'blueprint', and the word's meaning has shifted subtly to mean any design for the future, whether or not it is in photocopyable form." This process, called cyanotype photography, has found many uses since its invention by Herschel [169]. Figure 23 is an example of an early 20th century cyanotype.

Figure 23. Newspaper Row, New York, ca. 1900, cyanotype. Photo: Library of Congress, Prints & Photographs Division, Detroit Publishing Company Collection. Public domain.

Although its redox and light-sensitivity qualities make it an ideal blueprinting material, Prussian blue has a structural feature that lands it squarely in the domain of pharmacy and medicine. Because of its open crystal lattice and the fact that its monovalent counter ion can easily exchange with other monovalent positive ions, the pigment can harbor large singly positive ions, such as toxic thallium and cesium, making it an excellent sequestering agent for this type of poison. In its pharmaceutical guise, Prussian blue is marketed as a poison antidote under brand names such as Radiogolds, Antidotum and Thallii-Heyl and may be taken in capsule or powder form. The only side effect—hardly worrisome but more entertaining—is output in the form of spectacularly blue feces [163]!

Prussian blue's electrochromic properties have received a great deal of attention since they were first noted in 1978 [170]. Electrochromism (EC), a redox process, occurs in a substance when passage of an electric current provokes a reversible color change. Essentially color switching by loss or gain of electrons, Jöns Jacob Berzelius (1779–1848) first reported this phenomenon in 1815, when he described tungsten oxide's (WO_3) color change from pale yellow to deep blue upon reduction [171]. In 1969, S.K. Deb documented the first EC device using tungsten oxide [172].

Among Prussian blue's first commercial applications were switchable rearview automobile mirrors and voltage-regulated dynamic windows [173]. Among its many other applications are energy storage systems [174,175], biomedical [176] and clinical applications [177,178], transparent [179] and desalination batteries [180], sensors [181] and electrocatalysis [182].

As if this sampling of Prussian blue's versatility were not enough, a news item in the ACS's *Chemical and Engineering News* reported on a startup company, Natron Energy, which is designing safe and reliable batteries based on Prussian blue as both the anode and the cathode. Although these batteries may not have the power density to replace lithium-ion systems, they are reliable substitutes in applications that require quick power discharge, such as small electrical grids [183]. Prussian blue has come into its own as a thoroughly modern substance valued not only for its chromaticity but also for its electron transfer properties.

8. Structural Color: From Early Photography to Plasmonic Pigments

The uncanny connection in pigment usage spanning millennia can also be illustrated by another kind of artistic endeavor: the use of ordered arrays to produce structural color. First devised in an evolutionary process by Mother Nature and best observed in the shimmering iridescence of a peacock's plumage or a butterfly wing (Figure 24), it was first exploited commercially by the semiempirical photographic process known as daguerreotyping.

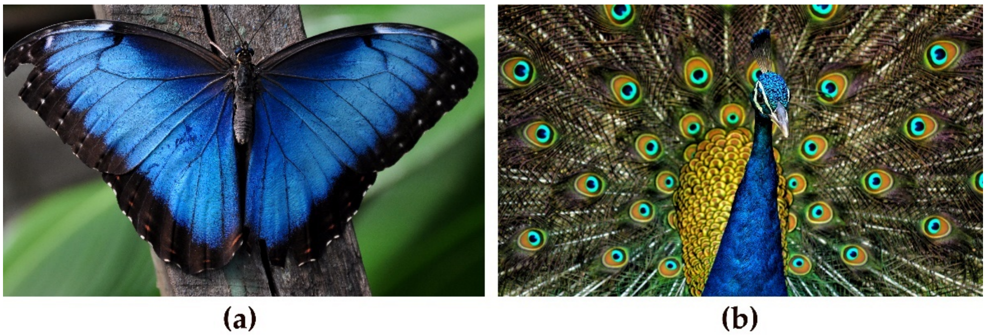

Figure 24. Structural color in animals. (**a**) Blue Morpho butterfly (*Morpho peleides*); photo: Derkarts. (**b**) Indian peafowl (*Pavo cristatus*); photo: Jatin Sindhu. The colors are due to the interference pattern of the incident light striking the thousands of orderly parallel microlamellae in the animals' structures, much like light striking a grating.

Daguerre was the quintessential experimentalist but had no idea of the theoretical basis of his results. What Daguerre was dealing with was structural color, a phenomenon that differs from the ordinary color of pigments. Pigments selectively absorb certain wavelengths of incident light; the unabsorbed light is reflected and accounts for the color perceived by the observer. The mechanism for structural color is quite different; it depends on an array of nanoscale structures equivalent in size to the wavelength of light, which selectively scatter the incident light into waves that interfere with each other both constructively and destructively in different directions. The colors of light that we see are the reinforced wavelengths that appear to us as iridescent or brightly colored.

This phenomenon has been in plain sight since the dawn of creation, but the first record of a systematic microscopic investigation of its cause was that of English polymath Robert Hooke (1635–1703), who discovered that small, thin plates, "almost like a company of sloping ridge or gutter tyles", cover peacock feathers and tinge the light "in a most curious manner and by means of various positions in respect of the light, they reflect back now one colour, and then another, and those most vividly" [184]. He also postulated that the destruction of the color when the feathers were immersed in water was due to insinuation of water between the ridges, thus preventing the light from traveling the way it did in air. Isaac Newton (1643–1727) came to a similar conclusion: that the feathers' colors were due to "thin plates" in their structure [185]. Although Hooke's peacock was not available, the painted lady butterfly (Figure 25) is an excellent substitute to illustrate his observations [186].

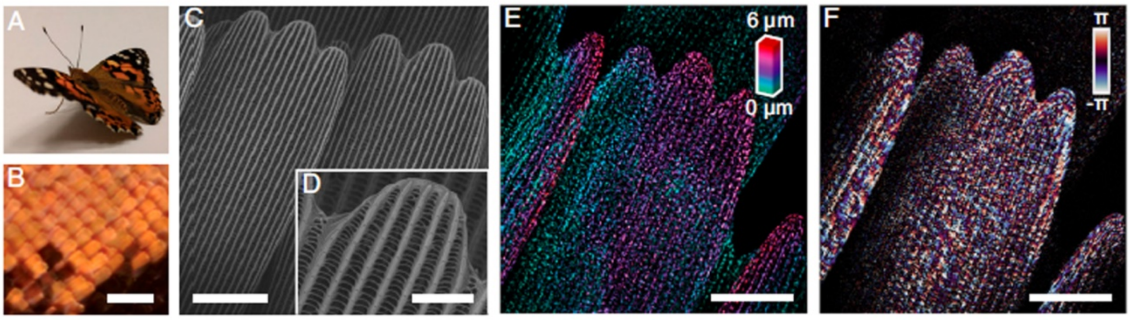

Figure 25. Imaging the structure of fully formed butterfly scales. (**A**) The painted lady butterfly, *Vanessacardui*. (**B**) Optical micrograph of orange and black wing scales. (**C**) Scanning electron micrograph of individual adult scales, with ridges running down the length of the scale. (**D**) Magnification of scale finger showing that ridges consist of stacked lamellae connected by crossribs. (**E**) Volumetric image of an adult scale acquired by speckle-correlation reflection phase microscopy (red, top of the volumetric data stack; green, bottom). (**F**) A single slice of phase data for the same scale. (Scale bars: (**B**) 200 μm; (**C**) 20 μm; (**D**) 5 μm; and (**E**,**F**) 20 μm) Reproduced from Ref. [186] under Creative Commons Attribution-NonCommercial-NoDerivatives License 4.0 (CC BY-NC-ND).

However, understanding the cause of structural color required a wave theory of light. In the early twentieth century, Lord Rayleigh developed a model that explained structural color as arising from constructive interference of light reflected from the top and bottom of films, the thickness of which was half the light's wavelength. Rayleigh's model was able to explain iridescence in structures containing ordered arrays of pores with spacings consistent with the observed colors—different colors for different viewing angles because of different spacings between the ordered arrays [187,188]. Today, physicists have developed tools to overcome the angle-dependent difficulty so that structural colors can be perceived to be the same at any viewing angle, allowing for more controlled applications for this phenomenon [189].

After decades of experimentation, Louis-Jacques-Mandé Daguerre (1787–1851) revealed his process to the world [190], and for the following 25 years, it remained virtually the only viable photographic process, although long exposure times made it difficult to sit for portraiture. The chemical basis was a multistep process: (1) Exposure of a highly burnished silver-plated copper sheet to iodine vapor to form a light-sensitive surface of silver iodide:

$$2\text{Ag (s)} + \text{I}_2 \text{ (g)} \rightarrow 2\text{AgI (s)} \tag{4}$$

(2) The sensitized plate was placed in a light-tight camera for subsequent exposure to form the latent image,

$$\text{AgI (sensitized)} \overset{h\gamma}{\rightarrow} \text{AgI (latent image)} \tag{5}$$

which was then (3) developed by exposure to mercury vapor to form a silver–mercury amalgam, thus completing the reduction of the silver halide:

$$2\text{AgI (latent image)} + \text{Hg (g)} \rightarrow 2\text{Ag, Hg (mercury amalgam)} + \text{I}_2 \text{ (g)} \tag{6}$$

The final fixing process dissolves the unexposed silver salts with an aqueous solution of sodium thiosulfate, $Na_2S_2O_3$, to form, it is thought, the complex $Na_3[Ag(S_2O_3)_2]$ [191,192].

Although Daguerre's invention has been downplayed as being only a bypath in the evolution of the modern photographic process [193], its importance, in our regard, is the fact that the finished product consisted of an ensemble of metallic nanostructures, the collective light-scattering properties of which were responsible for the optical properties of the daguerreotype. Regardless of the variability of the nanoparticle sizes, their orderly array allows for the collective oscillations of mobile electrons, called plasmons, to interact strongly with light, thus explaining the extraordinarily high resolutions of daguerreotype images, as well as pointing the way for the development of plasmonic color technology [194]. Because plasmonics can reproduce the yellow, magenta and cyan color space in ultrahigh resolution [195], they can be formulated as plasmonic pigments for incorporation into a variety of colorants, such as inks, paints and cosmetics [196,197] (Figure 26).

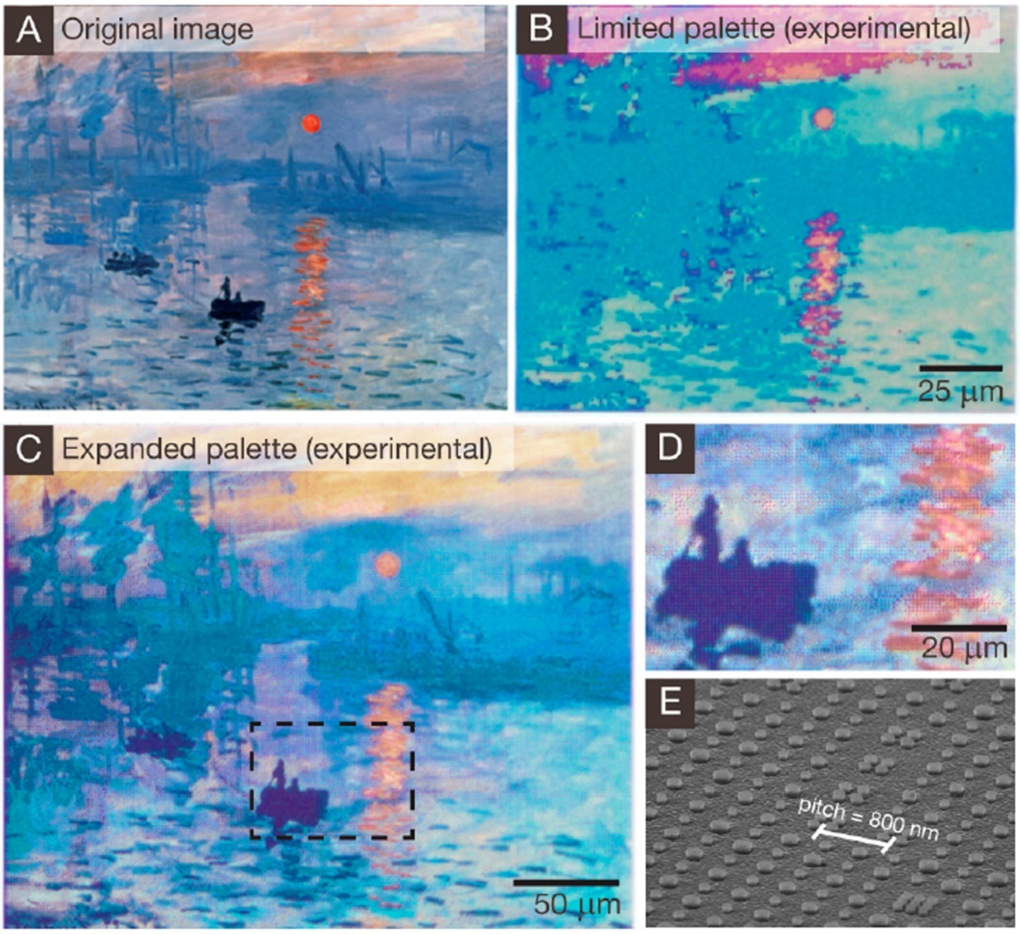

Figure 26. Plasmonic colors. Reproduction of *Monet's Impression, Sunrise* (Musée Marmottan Monet) using the expanded palette by color toning and mixing strategies. (**A**) Original input image; (**B**) reproduction using only the limited palette of "primary plasmonic colors", falling short of the original image; (**C**) realistic reproduction of the artwork using an expanded palette of colors, allowing for the subtle variations in tone and color in the original to the replicated; (**D**) higher magnification image of the dotted box in (**C**) highlighting the brush strokes that are resolved in the plasmonic painting; (**E**) tilted scanning electron microscope image of pixels showing how the colors observed in the plasmonic painting are the manifestation of a predefined structural layout. (Reprinted with permission from Ref. [197]. Copyright 2014. American Chemical Society).

Because they display unique optical properties, such as strong reflectance, resistance to bleaching and iridescence, the future looks bright for new formulations of plasmonic pigments. In addition, the range of possible applications of plasmonic materials is being systematized by the creation of plasmonic materials libraries [198].

9. Conclusions

Our four-dimensional journey through space and time is one that will never be concluded. For as long as human beings can work with a substance, they will never put it down until it has been put through all its paces. Every colorant we have examined here had, once upon a time, a single function: to color something else, be it a surface, a textile or a glass. It was valued for its singular ability to selectively absorb a wavelength range of visible electromagnetic radiation.

Extraction and synthesis strategies ensued, driven (consciously or not) by our capacity to perceive colors. A key component of almost every work of art is color, a property that remained associated intimately with the material in which it inhered; how it was produced stretched the practitioner's versatility to the limit. The discovery of new colorants also went hand in hand with the discovery of the elements, particularly in the area of pigment production.

Largely the products of oral, and later, written traditions handed down through hundreds of generations, they now follow the systematic pattern set by Isaac Newton (1643–1727) in 1666. The ancient Greeks and, in particular, Aristotle (384–322 BCE) made the first important contribution to what is now the modern theory of selective absorption of colors [199]. Then, separated by many centuries, both the Roman stoic philosopher Seneca (4 BCE-65 CE) and Leonardo da Vinci (1452–1519) noted the rainbow of colors generated by a prism and a glass full of water. However, it was left to Newton to formulate modern color theory by experiment; he succeeded in dissecting sunlight into Seneca's "prismatic" colors and then recombining them to form sunlight again. With this experiment, Newton initiated a systematic investigation of a colorant's nature, followed by a purposeful and equally systematic exploration of the theoretical and practical implications arising therefrom [200]. However, as we have demonstrated in this essay, serendipity seems to trump systematicity every time. It was by sheer serendipity that Egyptian blue's luminescence was discovered. No matter how systematically they labored, scientists were stumped by the nature of Maya blue for almost sixty years. More information on Purple of Cassius required the invention of two new instruments. Synthetic ultramarine and Prussian blue were lucky accidents exploited by prepared minds. Even the discovery of the first commercially viable route to synthetic indigo was the result of sheer accident. Therefore, systematics may be the first step in any investigation, but the wary and observant investigator who follows up by bridging gaps will always have the advantage.

We have also observed that human vision and ingenuity, coupled with the development of sensitive analytical instruments, have transformed these materials into workhorses for numerous applications in almost every field of human endeavor based upon properties valued only within the past few decades: infrared luminescence; semiconducting; the ability to form nanoparticles, nanoclusters and nanocages—and so much more. Some pigments were so far ahead of their time that even today, they serve as models for the advancement of materials science, and the very existence of some of them changed our preconceived notions about the nature of matter. The examples presented herein are not, by any means, exhaustive; there are so many more materials of cultural significance that have a colorful past and an exciting future. We have only begun to scratch the surface.

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3. Brunel, E.; Chauvet, J.-M.; Hillaire, C. *The Discovery of the Chauvet-Pont d'Arc Cave*; Éditions Équinox: Saint-Remy-de-Provence, France, 2014.
4. The fact that most of the selected pigments are blue is largely coincidental. However, we note that many of the iconic blue pigments have received a great deal of attention in the recent literature.
5. The term lake is derived from lac, the solid excrescence of the Indian wood insect, *Laccifer lacca*, from which the word lacquer is also derived. The general chemical reaction for lake formation is as follows: Dye(aq) + $2KAl(SO_4)_2 \cdot 12H_2O(aq) + 3K_2CO_3(aq) \rightarrow 4K_2SO_4(aq) + 3CO_2(g) + \text{Dye} \cdot Al_2O_3(s) + 24H_2O(l)$.
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