Original article

X-ray and optical spectroscopic study of the coloration of red glass used in 19th century decorative mosaics at the Temple of the Emerald Buddha

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ABSTRACT

The Temple of the Emerald Buddha in Bangkok, Thailand is noted for its glass mosaic decorations on exterior walls and statuary. The original mosaic artwork dates to the early 19th century and is composed of variously-colored, mirrored glass pieces. In this work, we examine the chemical composition and optical properties of the red glass manufactured at that time. Through the use of X-ray and optical spectroscopies, we demonstrate evidence that the 19th century craftsmen produced “ruby-gold” glass, wherein the red coloration is caused by the dispersal of nanoscale metallic gold particles throughout the glass matrix.

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1. Introduction

Built in 1782, the Temple of the Emerald Buddha is the largest Buddhist temple in Bangkok, Thailand. During the reign of King Rama III (1824 to 1851), the temple was restored as additional halls, pagodas and towers were constructed. The temple renovation included the use of mosaics composed of thin, mirrored glass in place of the more traditional gold-on-red lacquer art to decorate external walls and pillars of the Ordination Hall enshrining the Emerald Buddha [1,2]. These decorative glasses, commonly called Kriab mirrors, are leaded glass containing from 10% to 50% lead by weight (see Table 1 and reference [3]). They were fabricated in glasshouses sponsored [4] by Thai royalty. They are thin (300 μm to 1000 μm), translucent, and variously-colored. Glass of all colors was coated with a reflective metal paste on their back surface and affixed to exterior surfaces of the Ordination Hall using natural latex.

The royal Glass Department Production was terminated during the reign of King Rama V (1868 to 1910). Thus, the Kriab glass has not been produced in Thailand in over 100 years. Scant records of the glass-making techniques remain. Eight manuscripts National Library of Thailand [5] titled in Thai as “Textbook of glass melting” belonged to Prince Pramoch, the Head of Glass Production Department of King Rama IV, and were later donated to the National Library of Thailand in 1915. The language in these records is archaic and difficult for the modern reader. Some information on glass fabrication can be interpreted from these sources [6], such as a list of raw materials which includes, tin, salt petter, gold, lead, red soil, bronze, white stone powder and coloring glazes. No details of the manufacturing process remain which are known to us.

Over decades and with exposure to 20th century air pollution, the adhesion of the glass pieces to the walls degraded. By the time of the latest restoration of the Temple, beginning in 1982, the integrity of the mosaics was compromised by the loss of significant numbers of glass pieces. Without ready means of reproducing glass in the original style, commercially-sourced glass mirrors were imported and used in restorations beginning in 1982. The modern and original glasses have several aesthetic differences, as shown in Fig. 1. The modern glass is thicker, differently colored, and more reflective than the original glasses. The conservators of the Temple are interested in future restoration to more closely resemble the original visual appearance. Scientists at the Synchrotron Light Research Institute, Thailand’s national synchrotron user facility, were asked to investigate [3] the composition of original Kriab mirror pieces from the Ordination Hall.

In this paper, we examine original specimens of red-colored glass from the Temple. The physical mechanism by which small, spherical, metal inclusions drive the coloration of glass has been understood for over a century [7,8] with dispersed gold resulting in a red coloration. Some extant historical glasses are colored red by
Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>KMHR1</th>
<th>KMSR2</th>
<th>KMHCL2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO²</td>
<td>37.99 (9)</td>
<td>37.59 (77)</td>
<td>68.42 (42)</td>
</tr>
<tr>
<td>TiO²</td>
<td>&lt;0.15</td>
<td>&lt;0.15</td>
<td>&lt;0.15</td>
</tr>
<tr>
<td>Al²O³</td>
<td>1.41 (9)</td>
<td>1.20 (13)</td>
<td>1.71 (8)</td>
</tr>
<tr>
<td>Fe²O³</td>
<td>0.37 (5)</td>
<td>0.31 (4)</td>
<td>1.37 (7)</td>
</tr>
<tr>
<td>MnO</td>
<td>&lt;0.15</td>
<td>&lt;0.15</td>
<td>1.01 (5)</td>
</tr>
<tr>
<td>MgO</td>
<td>0.53 (12)</td>
<td>0.56 (11)</td>
<td>0.65 (15)</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>46.33 (103)</td>
<td>51.77 (124)</td>
<td>1.27 (3)</td>
</tr>
<tr>
<td>CaO</td>
<td>0.94 (4)</td>
<td>0.90 (8)</td>
<td>8.45 (7)</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.86 (5)</td>
<td>3.86 (14)</td>
<td>12.96 (28)</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.78 (1)</td>
<td>0.81 (3)</td>
<td>1.09 (2)</td>
</tr>
<tr>
<td>Sum</td>
<td>92.20 (103)</td>
<td>97.01 (131)</td>
<td>96.92 (31)</td>
</tr>
</tbody>
</table>

the presence of dispersed, nanoscale gold and called “ruby-gold” glass. The most famous example is the Lycurgus Cup, a Roman artifact dating from the fourth century C.E. [9] which is a brilliant red when seen under transmitted light. Lost in Europe during the middle ages, this coloration technique remained used throughout the Arab world during that period [10]. It was rediscovered and widely used in Europe beginning in the seventeenth century [10,11]. Small gold particles can be dispersed in glass by adding either hydrous chlorauric acid (HAuCl₄ × H₂O) or potassium auricyanide (KAu(CN)₂) to the molten glass followed by a reducing agent such as SnO₂, along with control of redox conditions as the glass is annealed [12]. The reducing agent serves as an electron source, reducing the gold to its zero-valent state. As the glass cools and anneals, spherical inclusions with diameters in the range of 20 nm to 100 nm are dispersed throughout the glass. This mechanism has been inferred [13] as the source of the red coloration of similar period glasses from Thailand on the basis of the presence of gold in proton-induced x-ray emission (PIXE) spectra, but has not been demonstrated quantitatively.

Hasbeek et al. [12] explain how a reducing agent such as SnO₂ added to a glass melt along with a gold salt can act as an electron source, reducing the gold to the metallic nanoparticles responsible for red coloration. To test the conjecture that mid-nineteenth century Thai craftsmen may have used a similar technique to make red glass, we have performed a chemical analysis using wavelength and energy dispersive X-ray spectroscopy (WDX/EDX) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to determine concentrations of major, minor, and trace elements in the glasses. We then applied X-ray and optical spectroscopy methods to characterize the gold content of our red glass samples.

In this paper, we demonstrate that gold is present in these red glass specimens in a metallic form and in a size and concentration known to produce red coloration. We discuss other possible coloration mechanisms, but conclude that gold is the principle coloring agent of these glasses.

2. Experimental methods

The glass samples studied here were obtained from the Thailand Bureau of the Royal Household [4] and come from different locations around the Temple. Sample KMHR1 was a hexagonal piece originally from one of eight inner pillars of the Ordination Hall and part of a pattern like the one shown on the left of Fig. 1. It was removed from the pillar at the time of a restoration effort in 1982. The piece measured by X-ray and optical spectroscopy is one of three pieces cut from the hexagon and used for different analyses. It is about 5 mm by 12 mm and 600 μm thick. Sample KMSR2 was removed a mosaic pattern like the one shown in Fig. 1 decorating a damaged piece of a concrete wall and housed in the Museum of the Temple of the Emerald Buddha. It is approximately square, about 8 mm on a side, and 960 μm thick. Both samples were cleaned with ethanol prior to X-ray and optical measurements. The samples are shown in the inset to Fig. 3.

Both pieces have weathered surfaces on the sides shown in Fig. 3 and both pieces are partially covered on the reverse side by the oxidized remains of the tin-lead alloy used to make the reflective Kirib mirrors. Both pieces have sharp edges indicative of having been formed into mosaic pieces by scoring and breaking, rather than by cutting while in a hot, softened state. Finally, both pieces are uniformly colored throughout their bulk.

X-ray Absorption Spectroscopy (XAS) data at the gold L₃ edge (11919 eV) were measured at beamline X23A2 at the National Synchrotron Light Source at Brookhaven National Laboratory in New York, USA. This is an unfocused bend magnet beamline using a Si(311) monochromator of a fixed-exit, Golovchenko–Cowan [14] design. Harmonic rejection is made by a single bounce, flat, Rh-coated mirror. An argon-filled ionization chamber was used as described below to measure the intensity of the incident beam, which was about 10⁹ photons per second in a spot of 1.5 mm in the horizontal and 0.5 mm in the vertical. At this low flux density, radiation induced changes in speciation are rarely observed, even in hydrated samples. No such changes were observed in the data presented here or in any other XAS measurements made on the Kirib glasses. A four-element, Si-drift, energy-discriminating detector was used to measure the X-ray fluorescence intensities. All fluorescence XAS spectra were corrected for dead-time using the algorithm of Woicik et al. [22].

Because the glass pieces have very low concentrations of gold, the XAS data were measured in the fluorescence geometry. The glass pieces are, however, too thick to allow transmission of the beam at the energy of the Au L₃ edge for the purpose of measuring a reference for energy calibration. Given the large number of scans measured on each sample and the relatively poor angular repeatability of the monochromator, measurement of an energy calibration reference is essential. To do this, we replaced the standard ionization chamber used to measure the incident intensity, I₀, with the argon-filled, four-channel, ionization chamber described by Ravel et al. [15]. This is shown schematically in Fig. 2. Using the same slit assembly described in that paper to define the multiple incident beams, the two central channels were blocked at the slit assembly using lead tape. This left the inboard and outboard beams, which are separated by 14 mm, for use in the experiment. The sample was placed in the path of the outboard beam, which was used to measure the fluorescence. The inboard beam passed beside the glass sample unimpeded, then struck a gold foil through

Fig. 1. Original Kirib glass mosaic on a piece of concrete wall on display in the Museum of the Temple of the Emerald Buddha. (Inset) Examples of modern, commercial glass used in 20th century restorations.
which transmission XAS was measured using a standard nitrogen-filled ionization chamber. This foil spectrum was used as the energy reference. The incidence and measurement signals for the fluorescence and reference samples were thus measured independently and simultaneously.

The low gold concentrations required many repetitions of the XAS scans on each sample. Forty-two scans were made on sample KMHR1, while thirty scans were made on sample KMSR2. The raw data were processed, aligned, and calibrated against the reference measurements using the Athena program [16]. The difference spectrum analysis described in Sec. 4 was also performed using this program.

Cu K-edge (8979 eV) XAS spectra of the red glasses were acquired in fluorescence mode at the beamline BL8 [17] of the Synchrotron Light Research Institute in Nakhon Ratchasima, Thailand. The incident beam is unfocused, monochromated by Ge(220) double crystals, 10 mm in the horizontal and 1 mm in the vertical with flux of about 10⁸ photons per second. The incident beam intensity was measured by an ionization chamber filled with a mixture of nitrogen and helium gases. The fluorescence signal was measured using a 13-element germanium energy-discriminating detector and corrected for dead time. The samples were in air during the measurements. A Cu foil was used for energy calibration. Copper (I) oxide and copper (II) oxide were used as references for copper speciation. A colorless glass (KMHCL2) of the same era was collected from the same pillar as the sample KMHR1 was also measured at the Cu K-edge. XAS spectra from the glass samples were averaged from 6 to 10 scans.

Optical transmission measurements were performed using synchrotron light at beamline U10 of the National Synchrotron Light Source. A Bruker Vertex 80v Fourier transform spectrometer equipped with a UV-visible CaF₂ beam-splitter was used in combination with both GaP and Si photodiode detectors to span photon energy ranges from about 1 eV up to 3.5 eV. One surface of the glass samples had the oxidized remnants of the metal used to mirror the glass. This material blocked some of the light passing through the sample, but did not show any specific features in the visible spectral region.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Minor and trace elements determined by LA-ICP-MS [mg/kg]. Uncertainties are discussed in the text.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KMHR1</td>
</tr>
<tr>
<td>Ti</td>
<td>212(5)</td>
</tr>
<tr>
<td>Mn</td>
<td>416(8)</td>
</tr>
<tr>
<td>Cu</td>
<td>2204(36)</td>
</tr>
<tr>
<td>Zn</td>
<td>82(2)</td>
</tr>
<tr>
<td>As</td>
<td>3234(35)</td>
</tr>
<tr>
<td>Rb</td>
<td>56(2)</td>
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<tr>
<td>Sr</td>
<td>21(1)</td>
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<tr>
<td>Zr</td>
<td>20(1)</td>
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<td>Ag</td>
<td>14(1)</td>
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<tr>
<td>Sn</td>
<td>77(3)</td>
</tr>
<tr>
<td>Sb</td>
<td>60(1)</td>
</tr>
<tr>
<td>Ba</td>
<td>91(1)</td>
</tr>
<tr>
<td>Au</td>
<td>45(1)</td>
</tr>
</tbody>
</table>

3. Chemical analysis

Small pieces of KMHR1, KMSR2, and KMHCL2 were cut and mounted in the two component resin Technovit 5071 (Heræus Kulzer GmbH) for chemical analysis. The resin mounted sample was polished and cleaned in an ultrasonic bath of de-ionized water. Possible surface contamination can be excluded since the first few seconds from the laser ablation signal, where the surface is ablated, is excluded by default from quantification.

Concentration of major elements expressed as simple oxides, including SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, PbO, Na₂O, and K₂O, were determined by a JESOL-6310 scanning electron microscope equipped with an Oxford EDX and a Micrscopy WDX spectrometer at the Institute of Earth Sciences University of Graz, Austria. These results are shown in Table 1. Samples were coated with carbon and a conductive film was used to make electrical contact with the aluminum sample holder. Analytical conditions were set to 15 kV accelerating high voltage and a sample current of 6 nA. A defocused beam (about 6 μm x 10 μm spot size) was used to minimize loss of volatile elements such as sodium. Lead and sodium were analysed by the WDX spectrometer, which has a typical mass fraction detection limit of 0.05. All other elements, shown in Table 2, were analysed by the EDX spectrometer with a mass fraction detection limit of 0.1 to 0.15. Natural mineral standards and the BCR-2G glass from the USGS [18] were used for standardization: Si (BCR-2G), Ti, Ca (titane), Al, K (adularia), Fe (BCR-2G), Mn (rhodonite), Mg (BCR-2G), Na (jadeite), Pb (galena). The BCR-2G reference material was analysed for quality control at the beginning, and in the middle and at the end of the measurements of the glass samples. Major elements could be reproduced within certified values. Sulfur, chlorine and phosphorus contents were verified qualitatively by the EDX spectrometer, but no significant amounts were detected. The light elements, Li, Be, and B, cannot be detected using the EDX spectrometer and so were analysed by LA-ICP-MS. No significant amounts were detected. The totals of the constituents do not sum up to mass fraction 100%. The low totals are likely related to H₂O content in the glass or to a loss of Na during analyses despite the low current and defocused beam that were used. The uncertainties of the oxide concentrations were determined from the standard deviation of 3 to 4 measurements at different spots on the sample.

Trace element concentration of the glasses was analyzed with a LA-ICP-MS system (Laser ablation unit: ESI NWR 193; ICP-MS: Agilent 7500) at the Central Lab for Water, Minerals and Rocks, NAWI Graz, Karl-Franzens-University Graz and Graz University of Technology, Austria. The material was ablated by using a 193 nm laser pulsed at 9 Hz, 75 μm spot size with an energy of 6.5 J/cm². Helium was used as carrier gas at 0.8 L/min flow and data were acquired in time resolved mode. For each analysis, a gas blank was obtained for background correction. The laser was active for 60 seconds followed
by 50 seconds washout time. The standard glass NIST610 [19] was 
routinely analyzed for standardization and drift correction while 
standards NIST612 [19], NIST614 and BCR-2 [20] were analyzed 
as unknowns to monitor the accuracy of the measurements. All 
standards could be reproduced within ±10% of the certified values 
[19,20]. Silicon was used as an internal standard. The uncertainty of 
the oxide concentration was determined from the standard deviation 
of 3 to 5 measurements at different spots on the sample.

4. Spectroscopic results

4.1. Au L\textsubscript{III} edge XAS

The X-ray fluorescence spectrum measured from sample 
KMHR1 is shown in Fig. 3. The XRF spectrum of sample KMSR2 is 
substantially identical. Along with various trace transition metals 
commonly found [3] in these glasses, we find a substantial amount of 
arSENic and a trace quantity of gold. Arsenic is a common con-
taminant [21] in natural galena (lead sulfide, PbS), a possible source 
for the lead in abundance in these glasses. (Lead is not seen in 
Fig. 3, which shows measurements with the incident beam below 
the Pb L\textsubscript{III} edge energy of 13035 eV.) The presence of As is a com-
pliCating factor in these measurements. The As K-edge is 11867 eV, 
only 52 eV below the Au L\textsubscript{III} edge at 11919 eV. As a result, every 
XAS scan through the Au L\textsubscript{III} edge passes through the As K-edge as 
well. The Au L\textsubscript{II} and As K\textsubscript{II} lines are separated by 800 eV, however 
the energy resolution of the detector [22] is about 250 eV when run 
with a 100 microsecond shaping time to minimize pile-up in the 
measured signal. With this energy resolution and the abundance of 
As relative to Au, the tail of the As K\textsubscript{II} peak contributes significantly 
to the spectral weight in the energy range of the Au L\textsubscript{II} line. The Cu 
K\textsubscript{II} peak at 8904 eV is also present. While this is a similar separation 
from the Au L\textsubscript{II} peak at 9713 as the As K\textsubscript{II} peak at 10543 eV, 
the Cu signal is not changing during the measurement, thus is only 
a constant contribution to the background.

The extent of the contamination of the Au XAS spectrum by the 
much larger quantity of As in these glasses is seen in the top panel of 
Fig. 4. The principle step in these data occurs at the position of 
the As K-edge. In the second panel, these data are treated as As K-edge 
data for the purpose of normalization and are shown along with As 
K-edge data from the same sample measured properly – i.e. with the 
discriminator window of the detector set around the As K\textsubscript{II} peak.

The same As white line is measured in both spectra. However, 
excess spectral intensity is observed above the Au L\textsubscript{III} edge in the 
spectrum measured with the discriminator window around the Au 
L\textsubscript{II} peak. The problem, then, is to extract an interpretable Au signal from 
these data.

A difference spectrum is computed by subtracting the properly 
measured As K-edge data from the current spectrum. This is shown 
in the third panel of Fig. 4. The resulting difference spectrum shows 
a distinct jump at 11919 eV, the energy of the Au L\textsubscript{III} edge. The spu-
rious point at 11878 eV is an artifact of interpolation. The As K-edge 
data used to make the difference spectrum were measured on a fine 
energy grid through the edge and white line while the energy grid 
of the Au L\textsubscript{III} measurement was much more sparse in that energy 
range.

The difference spectrum is treated as a XAS spectrum. The result 
of this normalization is shown in the bottom panel along with a 
XAS spectrum measured on a gold foil in transmission. While the 
extraction is unreliable above 12000 eV, the difference spectrum is 
clearly dominated by the XAS signal from metallic gold. The XAS 
spectra of bulk and colloidal gold [23] are known to be nearly identi-
ical. Performing the same analysis on sample KMSR2 resulted in 
a difference spectrum likewise dominated by the XAS signal from 
metallic gold.

4.2. Cu K-edge XAS

Red glass can also be colored by copper [24,25] or by selenium 
[26], both of which are common red colorants in contemporary 
glass. While the glasses studied here have copper in much 
higher concentration than gold, selenium is not present within the 
∼1 mg/kg detection limits of the LA-ICP-MS and X-ray fluorescence 
spectroscopy presented.

Copper offers two plausible mechanisms for the red coloration of 
these glasses. Cuprite, monovalent Cu\textsubscript{2}O, is a brilliant red crystal 
with coloration controlled by optical absorption arising from transfer 
of charge from the O\textsuperscript{2−} anion to the Cu\textsuperscript{1+} cation. [27] Copper, 
like gold, has an optical response leading to a lustrous, yellowish 
color in the bulk metal. Like gold, it can act as a red colorant when 
present in glass as dispersed sub-100 nm metallic particles.

Cu K-edge (8979 eV) XAS spectra of the red glasses and the copper 
standards are shown in Fig. 5. The glass samples show the 
prominent peak at about 8983 eV corresponding to an electronic 
transition from 1s to 4p [28] characteristic of monovalent Cu\textsubscript{2}O. The copper 
in these glasses is clearly monovalent, like cuprite. However, 
monovalent copper in the glass has a filled d-band which 
precludes charge transfer and therefore precludes optical absorption 
[27]. That the colorless glass contains Cu in the same chemical 
state, albeit in lower concentration [3], as the red glass indicates 
that the Cu\textsuperscript{1+} species does not contribute to the coloration.

The glass samples show no evidence of metallic content in their 
XAS spectra. However, the same is true of Cu XAS measured on 
copper–rubie glasses, as discussed by Nakai et al. [33]. In that work, 
the authors concluded that the red coloration is due to dispersion of 
less than 5% of the Cu content as a metallic colloid, while the rest is 
the same non-color-forming Cu\textsuperscript{1+} species that we observe here. To 
derstand the roles of Au and Cu in the coloration of these glasses, 
we examine their optical spectrum.

4.3. Optical spectroscopy

Optical spectroscopy further confirms the identification of 
metallic gold particles dispersed throughout the glass and explains 
the red color of these samples. Fig. 6 shows the optical absorbance 
spectrum A of sample KMHR1, which is related to the measured
transmission $T$ by $A = -\log_{10}(T)$. The absorbance of sample KMSR2 was essentially identical, except for an overall lower optical transmission due to more residual opaque adhesive on the back side.

The absorption spectrum of Fig. 6 is typical of small (∼100 nm diameter), spherical, metallic gold particles embedded in a host matrix of glass [30]. This general behavior was first explained by the effective medium theory of J.C.M. Garnett [7,8]. Garnett was specifically interested in explaining how various metals in glass produced distinct colors. His theory for the effective optical response $\varepsilon_{\text{eff}}$ of a composite material consisting of spherical particles with dielectric response function $\varepsilon_a$ embedded in a host material having dielectric response $\varepsilon_b$ takes the form [31]:

$$\varepsilon_{\text{eff}} = \varepsilon_b + \varepsilon_b \frac{3f (\varepsilon_a - \varepsilon_b)}{(1-f)(\varepsilon_a - \varepsilon_b) + 3\varepsilon_b},$$

where $f$ is the volume fraction occupied by the spherical particle inclusion. In the case of colored glass materials, the volume fraction of metal particles is typically less than 0.1%. In the limit of small $f$, the average response can be approximated as:

$$\varepsilon_{\text{eff}} = \varepsilon_b + \varepsilon_b \frac{3f (\varepsilon_a - \varepsilon_b)}{\varepsilon_a + 2\varepsilon_b},$$

indicating a resonance condition can exist when $\varepsilon_a = -2\varepsilon_b$. From this effective dielectric response, one can calculate the complex refractive index $n = \eta + ik = \varepsilon^{1/2}$ from which standard optical quantities such as the reflectance and absorption can be determined.

A consequence of the large density of conduction electrons in metals is a characteristically large and negative dielectric response at low frequencies, increasing with frequency, and crossing over to positive at what is known as the plasma frequency. A typical glass has $\varepsilon_b \approx 2.25$ (for a refractive index $n \approx 1.5$) and thus, when the metal’s dielectric response reaches $\varepsilon_a \approx -4.5$, a resonance absorption occurs. For gold [32], this happens at a photon energy of $2.3$ eV (539 nm), resulting in the absorption peak at that energy. Since the frequency where $\varepsilon_a = -2\varepsilon_b$ depends on the metal, the position of this small particle resonance serves to identify the type of inclusion.

We attempted quantitative fits to the measured absorbance using the Garnett effective medium theory in combination with the known optical response for gold [32], recognizing that the dielectric response for the glass matrix can vary with the type of glass and its constituents. To this end, we approximated the host dielectric response as a wavelength-independent refractive index and allowed it to vary as a fitting parameter. We also attempted to
The measured response was approximately 5 for response ...

The results for a fit to the absorbance are shown in Fig. 6. As can be seen, the Garnett theory gives a very good fit to the position, strength and width of the absorbance peak near 2.3 eV assuming glass having n = 1.52 as the host material, a gold particle volume fraction of 2 x 10^{-5}, and a particle diameter on the order of 30 nm. However, the fit fails completely for photon energies near and above 3 eV. We suspect this may be from impurities in glass material itself. For example, iron is present (see Fig. 3) in these samples and Fe^{3+} ions result in absorption in the near UV [34]. Arsenic, also present in these samples, is another impurity [35] that could explain the near UV-absorption. Given that the human eye loses sensitivity in the violet and beyond, the red color of these glass tiles can be explained as being predominantly from the small gold particles, which absorb in the green and blue and which allow red light to pass with less attenuation. Subsequent direct measurements of the glass refractive index indicate n ≈ 1.65, consistent with the known high lead content. The difference from our fit value of n = 1.52 may be due to approximations used in developing the Garnett theory, or that the chemical process associated with reducing the precipitating gold particles leaves each one embedded in a glass shell having smaller n. A 2.7% increase in the gold plasma frequency also remedies the discrepancy.

Given the strong resonance in the measured data at 2.3 eV, it is impossible to fit the optical spectrum with only Cu. The upper plot in Fig. 6 shows the fit using an adjustable fraction of Cu. With 25% Cu by volume, a reasonable fit is found, although with this much Cu, the fitted function deviates from the measurement around the Cu absorption energy of 2.18 eV. While the fit including Cu is closer to the measured spectrum above the Au absorption peak, recall that no effort has been made to model the absorption of these glasses in the ultraviolet, which will certainly result in increasing absorption through the blue, indigo, and violet. We cannot exclude the possibility that some Cu exists in the form of metallic particles in this glass, but the amount relative to Au is certainly much less than the 25% considered by the calculation shown in Fig. 6.

5. Discussion

The coloration of the red glass pieces from the 19th century mosaics decorating the exterior of the Temple of the Emerald Buddha is controlled by small, metallic, gold particles dispersed in the glass matrix. XAS data measured at the Au L2 edge are consistent with metallic gold. Optical spectroscopy shows that the absorption properties of the glass are consistent with approximately 30 nm diameter gold particles dispersed in the glassy medium. While metallic copper might also contribute to the red coloration, the volume of metallic copper is much smaller than the volume of metallic gold.

Several redox active elements of the sort required for reduction of metallic nanoparticles [10] are present in the glass. Period documentation [5] identifies tin as an ingredient used in glass-making, so it is plausible that it was intentionally added as a reducing agent. We find small quantities of both tin and antimony as well.
as a substantial amounts of arsenic and iron. Tin and antimony cannot be seen in Fig. 3 because the incident beam in that figure is below the K-edge energies for those elements. Both are visible when the XRF spectrum is measured with a 31 keV incident beam and both are seen in the chemical analysis shown in Table 2.

The primary source documents [5] refer to both gold and tin – along with other, more cryptic ingredients – as constituents of glass made in Bangkok in the 1830s. These are the elements that are discussed by Haslbeck et al. [12] for modern recreation of ruby-gold glass. The use of tin or other metals as reducing agents for a noble metal in glass is extensively documented for historical glass-making over centuries and from Europe to Persia [10]. The conjecture that Thai glass-makers of the 1830s intentionally used the ruby-gold technique is well supported both by the material properties of the glass and by the limited historical documentation.

That said, many questions of an art historical nature remain about glass-making in Thailand in the early 19th century. Was ruby-gold glass-making an independently discovered craft or was it imported either from elsewhere in the region or the world? The existing documentation explains nothing about glass blowing and cutting techniques. Finally, little is known about sources of materials for these glasses. Haslbeck et al. [11] report successfully making ruby-gold glass starting from both hydrous chloroauric acid and potassium aurocyanide. In ancient Rome and in early modern Europe, gold was introduced to glass as chloroauric acid formed by dissolution of metallic gold in aqua regia [10]. This is a plausible mechanism for the introduction of gold into the red Kriab glasses.

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References

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