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An Ethnochemical Analysis: Red Glass Beads from the Eastern Region of Ghana

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Using a variety of spectroscopic methods, elemental compositions and coloring agents in recycled translucent red glass beads and red powdered glass beads from the Eastern Region of Ghana were investigated. The evolution of bead-making in Ghana was evaluated from an ethnochemical perspective by interviewing a series of experts, examining and collecting glass materials, and recording the conditions under which the beads were produced. The origin of bead-making in Ghana was traced to the Yoruba peoples of Western Nigeria. Combination of spectroscopic methods allowed for extensive qualitative and some quantitative analysis of the network formers, modifiers, and colorants used in red glass beads from Ghana while avoiding the use of HF. Red glass beads and dye from Ghana were found to contain quantifiable amounts of cadmium. The beads were composed of soda-lime silica glass wherein a portion of the Ca modifiers were replaced with Zn, correlating with procedures for the industrial fabrication of red glass. The structure of the beads and efficacy of metal extraction were found to be dependent on surface area interactions between particles during firing and digestion processes.

1. Introduction

1.1 What is ethnochemistry?

Ethnochemistry is the study of the knowledge of matter and its changes as it relates to a specific ethnic or cultural group; it concerns the implementation of chemical knowledge to adapt materials for the purpose of suiting societal needs. Ethnochemistry is separate from the study of physical anthropology which concerns the physio-chemical evolution of man and mankind.[1]

Bead-making in West Africa has been adapted to suit cultural and economic purposes for over a millennium, but the history of the practice and trade remains largely undocumented.[2] The history of glass-working and material development in sub-Saharan Africa is a heated topic between Afrocentric and Eurocentric anthropological debates; however, with an ethnochemical approach it is more practical to examine evidence and draw conclusions.[3]

A mixture of cadmium sulfide and cadmium selenide [Cd(S, Se)] was widely used in industrial fabrication of red glass; however, many cadmium compounds are outlawed globally due to their high toxicity to humans and the environment. Conversely, the traditional red glass colorants, copper and gold are safe for use; but, they are more expensive and require extensive, accurate heating processes, making them inconvenient for mass production. Red glass beads and dye from Ghana were found to contain quantifiable amounts of cadmium.

1.2 Afrocentric vs. Eurocentric Material Development in sub-Saharan Africa – Metallurgy

Metallurgic practices on the African continent are an important topic of debate in the history of material development: Researchers used ^{13}C-dating on iron slag from archeological sites to estimate the age of origination of iron-working in various geographic locations. [4, 5] The temperatures needed to anneal iron ore, fire pottery, and soften glass cannot be attained in a regular wood fire without the usage of a specialized kiln or some form of forced

draft.[5] Special attention to kiln construction has helped researchers form a clearer picture of material development on the African continent. [4, 5]

Diffusion theory dictates that the ancient Phoenician city of Carthage in North Africa served as an entrance point for the knowledge of iron smelting from Greece with archeological evidence dating to 600 B.C. Map 1.2 shows the Trans-Saharan trade routes between Northern and sub-Saharan Africa in the 14th century A.D., but the travel network existed prior to historic times with signs of early migration routes dating from 7000 B.C.! [6]

The earliest evidence of iron-smelting in sub-Saharan Africa was carbon-dated to ~500 B.C. and was linked to the Nok peoples of central Nigeria whose domain overlapped with the Yoruban peoples in the West.[4] One site was dated to around 1000 B.C. but needs further testing; however, it opens the possibility that the earliest Iron Age may have occurred in sub-Saharan Africa.[4, 5] The intervals of time between iron-ages in Northern and sub-Saharan Africa are relatively short, rendering the Diffusion theory improbable. It has been theorized the origins of iron smelting arose from the accidental introduction of iron ore into a pottery firing kiln. Ferruginous laterite, an iron-containing mineral, is abundant in the top-soil and in large underground deposits in most of West Africa; smelting of iron ore can occur at temperatures from 1100 °C to 1300 °C, the typical minimum temperature needed to fire most clays is around 1000°C.[4, 5]

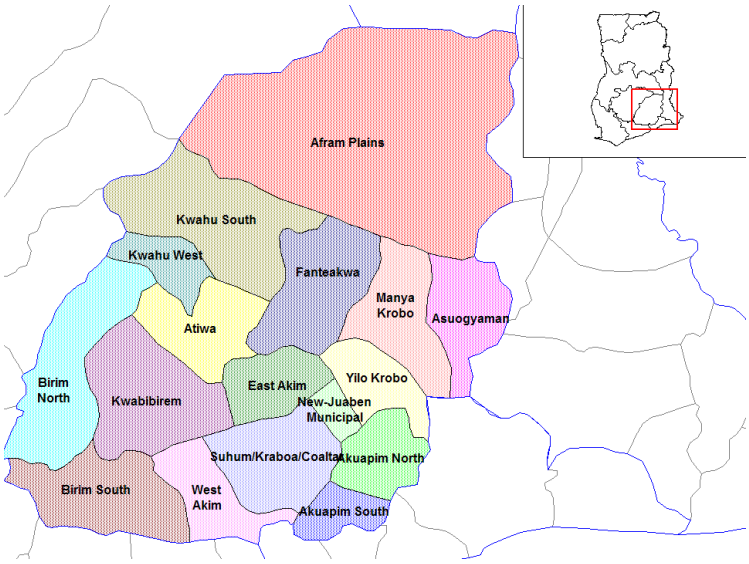
It is this knowledge of how to control and manipulate heat through kiln construction to comply with energy needs for making glass, firing pottery, or extracting, melting, mixing, and casting metals that suggests some commonalities and shared knowledge. For multiple people isolated from one another to discover laws of nature simultaneously is a common phenomenon in scientific history, making it difficult to trace and define origins. It can be agreed, an ethnochemical relationship exists between the craftsmen, their works, and societal needs.

Map 1.2) Trans-Saharan Trade Routes and the Krobo Migration c.a. the 14th Century A.D. [6]
The Krobo Migration Route of the early 1500's is shown in red; the highlighted route is 1092 km.

1.3 History of Bead-making in the Krobo Region of Ghana

The tradition of crafting beads from recycled glass has thrived in West-Africa since the 9th century A.D.; glass from Medieval European, North African, and "near-eastern" countries was imported via the trans-Saharan trade route in the form of glass bottles or glass beads and crafted into new, more marketable beads.[3, 7] Beads are symbolic of social stature in innumerable African cultures; the peoples of Ghana tell family histories and convey emotion through self-decoration using combinations of different types of beads.[2]

A notable center for glass bead-making developed among the Yoruba in the Ife region of Nigeria; although their practices can no longer be traced to a single ancestral root, the Krobo of Ghana have become the modern equivalent of this antiquated bead center. [3, 7] It is hypothesized the Dangme peoples of western Nigeria migrated to the mountainous Krobo region of Ghana sometime in the 1500's. Their migration route is shown in *Map 1.2*. [8] The Krobo peoples are the largest of the seven ethnic groups making up the Ga-Dangme linguistic group who comprise approximately 7.4% of the Ghanaian population; the Krobo districts of the Eastern Region are shown in *Map 1.3*.[9]



Map 1.3) Contemporary Districts, Eastern Region of Ghana[10]

Koforidua is the capital of the Eastern Region and lies on the Western edge of the Yilo-Krobo district. Odumase-Krobo is the capital of the Lower Manya-Krobo district. The distinction between Yilo and Manya Krobos is their times of migration; the Manya-Krobos were the first peoples and the Yilo-Krobos came some hundred years later.

1.3.1 powder glass beads

It has been suggested the practice of powdered glass bead (PGB) making in West Africa dates to between the 7th to 13th centuries; however, further research is necessary.[11] The famous Ghanaian bodom bead is made using the powdered glass method; little research has been done on ancient bodom beads due to their tremendous cultural and economic value. [2, 3, 11]

PGBs are made by pulverizing and sieving clear, colorless glass from broken windows or bottles. The fine glass dust is mixed with a powdered dye (*Fig. 1.3.1 left*) of the desired color in a ratio of about 1 part dye in 100 parts glass. In a kaolin-coated ceramic mold, the mixture is packed around a cassava stem; skillful layering of the colored glasses can be implemented to create complex designs relaying messages like social status and lineage in bodom beads. The cassava stem is burnt away during the firing process leaving a hole for stringing and a smooth, heavy opaque bead (*Fig. 1.3.1 left*).

Figure 1.3.1 Raw Red Glass Dye (left) and Red PGB (right)

Figure 1.3.1 shows raw red glass dye used to make PGB collected from Cedi Beads Industry (left); the bead shown on the right was collected from the Koforidua Bead Market.

1.3.2 translucent recycled glass beads

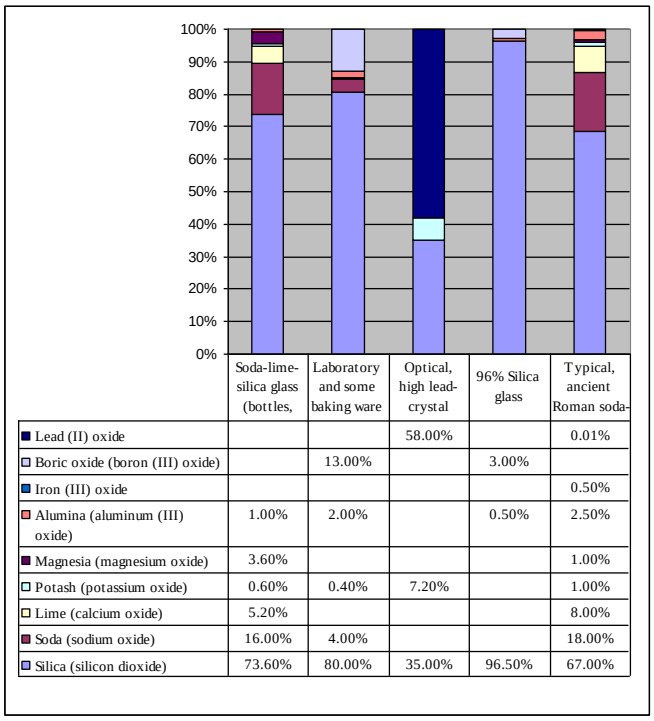
Translucent recycled glass beads (TRGB) are relatively modern in Ghana; most Ghanaians seem to prefer PGBs to the TRGBs, made using glass fragments approximately 0.125 cm^3 in size. Fragments containing the pigment of interest are placed in ceramic kaolin-coated molds and fired. The molds are removed from the kiln when the glass reaches its transition temperature (T_g); glass is a sort of polymer and when it is heated to the T_g range, it loses its rigidity, becoming rubbery. At the lower end of the T_g range, the particles begin to sinter wherein localized surface bonding between closely neighboring particles occurs. While the glass is hot and pliable, an iron pike is used to penetrate the glass and smooth the surface of the bead by rolling it against the walls of the mold. The product is a semi-translucent, rough textured bead.

Figure 1.3.2 Dark Red Raw Materials for TRGBs (left) and Red TRGB (right)

Fig. 1.3.2 shows dark red glass obtained from Cedi Beads Industry in Odumase, Krobo(left); TRGBs were purchased from Derek Kpabitey Tetteh in Odumase, Krobo (right).

1.4 What is glass?

Thousands of different types of glass have been manufactured throughout the ages to suit different purposes such as Pyrex® bake ware comprised of borosilicate glass. Fig 1.4 describes common types of glass and their relative compositions. The most common type of glass is soda lime silica. [5, 12, 13]



	Soda-lime-silica glass (bottles,	Laboratory and some baking ware	Optical, high lead-crystal	96% Silica glass	Typical, ancient Roman soda-
Lead (II) oxide			58.00%		0.01%
Boric oxide (boron (III) oxide)		13.00%		3.00%	
Iron (III) oxide					0.50%
Alumina (aluminum (III) oxide)	1.00%	2.00%		0.50%	2.50%
Magnesia (magnesium oxide)	3.60%				1.00%
Potash (potassium oxide)	0.60%	0.40%	7.20%		1.00%
Lime (calcium oxide)	5.20%				8.00%
Soda (sodium oxide)	16.00%	4.00%			18.00%
Silica (silicon dioxide)	73.60%	80.00%	35.00%	96.50%	67.00%

Figure 1.4 Common Glass Compositions[14]

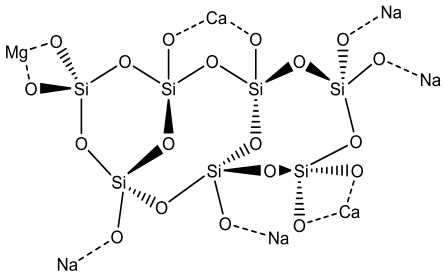


Figure 1.4.1 Glass Matrix Structure

1.4.1 a brief background on glass chemistry

Fig. 1.4.1 shows a typical structure for the soda-lime silica glass matrix. Network formers are defined as particles that maintain their bonding abilities in glass given their high affinities for oxygen; these include: Si, Ge, P, As, but silicon dioxide is the most widely used former.[12] Modifiers like Na, Ca, Cs, and K are used to form a chemically resistant, stable product. [12] More specifically, Na_2CO_3 and K_2CO_3 are fluxes, or materials that lower the melting point of the former(s). [5, 12, 14] A stabilizer, most often Ca_2CO_3 a.k.a. "limestone", aids in maintaining the structural integrity of the finished product; it prevents the glass from dissolving in water as it would otherwise decompose rapidly due to its polar nature.[5, 12] Al_2O_3 and MgO are also commonly used stabilizers.[12]

Glass has contributed to the development of various technologies throughout history, but what is glass really? Glass is an inorganic, semi-crystalline amorphous super-cooled liquid. [12, 13] This means that a portion of the atoms in glass are in a perfect geometric crystalline lattice structure and some are amorphous; they form the same bonds as the atoms in the crystalline structure, but do not form a perfect geometry. A super-cooled liquid is a substance below its freezing point and is "solid" but still subject to structural shifting.[5] In the context of this study, it is convenient to consider the glass matrix as a solvent and the colorants as a colloidal suspension.

The oldest written recipe for glass is from the library of the Assyrian King Ashurbanipal (669 –626 B.C.) and calls for 7 parts sand (mainly SiO_2), 2 parts ashes of sea plants (soda-ash [Na_2CO_3], or pot-ash [K_2CO_3]), and 1 part chalk (Ca_2CO_3). [15] Upon heating the raw materials to a temperature of approximately 1300 ºC, carbon dioxide gas forms and escapes, leaving oxides like CaO. [12] Logistically, it makes sense the recipe for glass could have traveled via the trans-Saharan trade-route to sub-Saharan Africa prior to European contact in the late 15th century A.D.

1.4.2 a brief background on red glass

Red glass has a notorious history in its difficulty to produce. Copper-ruby glass production dates to approximately 1500 B.C. in Egypt; some gold-ruby glasses date back to the Roman Empire circa the 9th century! [12, 15,] Copper and gold are striking pigments, or pigments that must undergo a secondary or extended heating process for colloidal color centers to form in the glass where Cu (I) and Au (I) undergo reduction to form metallic nanoparticles.[12, 15] *Fig. 1.4.2 i* shows the interaction of a noble-metal nanoparticle with a glass matrix. They are incredibly sensitive to the

batch-melt mixture, temperature, timing, and reduction-oxidation atmosphere making them impractical and expensive for industrial production. [15]

Cd(S, Se) glasses form color during the batch-melt and are less sensitive to their physico-chemical environments; the 1934 patent suggests replacing Ca with Zn as a network stabilizer, but a mixture of the two metals suffices. Additionally, a mixture of the sulfide and selenide are necessary for red color formation; Silverman suggests several synthetic routes for the development of red color during batch-melt.[16, 17] Over the last half-century, Cd(S,Se) mixtures have been used commercially to produce red glass in bulk due to their lower cost and relative ease of production. [15, 17] The use of Cd(S, Se) glass colorants is banned in many countries due to the toxicity of cadmium to humans and the environment.[15]

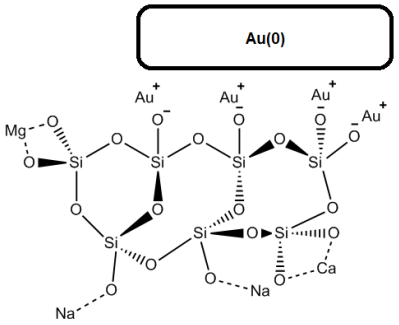


Figure 1.4.2 i) Gold Nanocrystal and Glass Matrix Interaction[18]

Figure 1.4.2 ii) Colloidal Suspensions of Au^0 Nanoparticles Showing Colorimetric Size Dependency[19]

The pigmentation of red glass is dependent on the size of the nanoparticles of gold, copper, and cadmium sulfide/selenide suspended in the glass matrix.[15] As with the solutions in Fig. 1.4.2 ii, over-heated red glass experiences greater nanoparticle aggregation during the secondary heat treatment and will acquire a liverish color with increasing opacity.[15, 16, 19] An energy-efficient and environmentally-friendly replacement for the cadmium sulfide/selenide colorants is a relatively new area of research with much work to be done. [15]

1.5 Review of Spectroscopic Methods in Glass Analysis

Glass is notoriously difficult to analyze due to its chemically resistant nature; hydrofluoric acid is the most commonly used solvent in analytical studies on glass as it completely dissolves the silica.[5,12,19] Hydrofluoric acid is considered highly dangerous to work with so a variety of analytical methods were employed with the interest of producing accurate qualitative and quantitative data without using HF.[20] Instead, extraction methods are used to manipulate the sol-gel chemistry and ionic nature of glass in order to isolate colorants from red glass beads.

1.5.1 UV/Vis

Meulebroeck et al. successfully utilized UV/Vis to elucidate information regarding ancient Roman glass beads.[21] This non-destructive method was able to differentiate between glass made in reducing or oxidizing furnace environments by producing shifts in the absorption peaks of iron and manganese compounds. Iron is a common impurity found in sand and manganese is used as a decolorizing agent, so these elements are present in a variety of glass.[12, 14, 21] Researchers were also able to determine the authenticity of the glass because commercially produced modern soda-lime glass exhibited an absorption pattern differing from ancient glass produced with potash. [21]

UV/Vis cannot be used to delineate glass containing cuprous oxide and elemental copper which absorb at practically the same wavelength in the visible region.[15] It may provide useful analytical data in determining the presence of colorants such as differentiating absorption peaks from copper, cadmium, and gold. UV/Vis was attempted in this study; however, no useful data was obtained. It may be worth future experimentation.

1.5.2 Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDX)

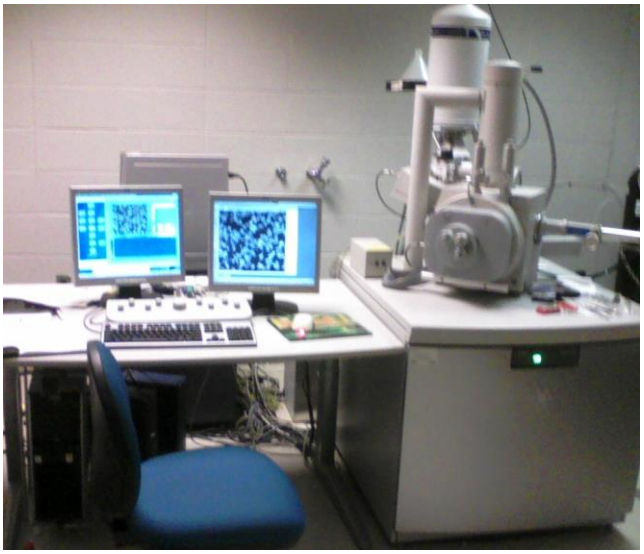


Figure 1.5.2 SEM – EDX, University of North Carolina at Asheville

SEM-EDX is a prominent technique cited in the field of glass analysis. It is semi destructive because surface particles from the sample become trapped within the conductive resin coating. [15] It can provide information regarding local elemental composition, oxidative states, and structure.[15] The SEM was used to image the surfaces of the beads and some of their raw materials, providing insight into the structure of the glass beads and conditions within the ovens in which they are made.

EDX was utilized to perform localized qualitative analyses on the beads in their whole and crushed forms. The EDX is limited in its quantitative ability to major components (>10 %w/w) by the energy dispersive spectrometer.[22] In this study, researchers successfully implemented EDX analysis by identifying the formers and modifiers of the glass matrix; however, colorant concentrations were too low to detect.

1.5.3 Powder X-ray Diffractometry (PXD)

PXD is valuable in structural elucidation and elemental analysis of crystalline solids and relies on constructive interference of X-Ray wavelengths of light between atomic planes of a crystal, a phenomenon known as Bragg's Law (Eqn. 1, Fig. 1.5.3).[23]

$$n\lambda = 2d\sin\theta \qquad (1)$$

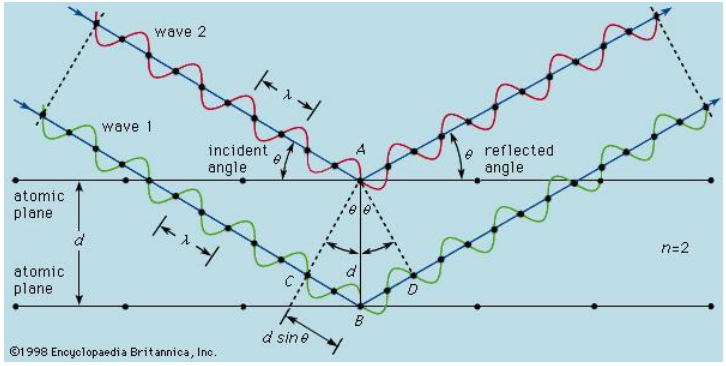


Figure 1.5.3 Bragg's Law[24]

PXD cannot typically be employed to analyze glass due to its amorphous character; however, it was successfully used to characterize the raw red dye comprised of entirely crystalline materials (*Fig. 1.3.1 right*).

1.5.4 Mossbauer spectroscopy

Unfortunately, the Mossbauer effect is not exhibited in copper and cadmium. Haslbeck et al. successfully utilized Mossbauer spectroscopy to identify both Au(I) and Au(0) in gold-ruby glass.[18] They examined the atomic gold particles on the surface of gold nanoclusters within the glass matrix by measuring nuclear excitation. It was determined the gold nanoclusters were responsible for producing color via surface plasmon resonance; whereas, the Au (I) remained bound in the glass matrix and did not emit light in the visible region. According to Johnson et al., it may be worth while to examine the glass using Mossbauer spectroscopy despite the lack of activity in Cu and Cd.[25] It is a topic for future research in this study.

1.5.5 Atomic Absorption Spectrophotometry (AAS)

AAS is not commonly used in the field of glass research due to the susceptibility of the glass nebulizer to chemical attack by hydrofluoric acid. Testing of ancient beads is not economically feasible due to the necessity of pulverizing the glass samples. Digestion methods of glass materials were explored in order to take advantage of the low limit of detection and accuracy in measuring metallic entities, dependent on the Beer-Lambert Law (Eqn. 2)[26].

$$A = \varepsilon \boldsymbol{\ell} [c] \rightarrow y = mx + b \qquad (2)$$

A = y = absorbance (AU)
$\boldsymbol{\ell}$ = path length (cm)
ε = molar absorptivity (mL μg^{-1} cm^{-1})
[c] = x = concentration ($\mu g\ mL^{-1}$)

$m = \varepsilon \boldsymbol{\ell}$ (mL μg^{-1})
$b = [c_0]\ \varepsilon \boldsymbol{\ell}$ (AU)
$[c_0]$ = blank ($\mu g\ mL^{-1}$)

2. Experimental Methods

2.1 Interviews and Collection of Oral Histories in Ghana

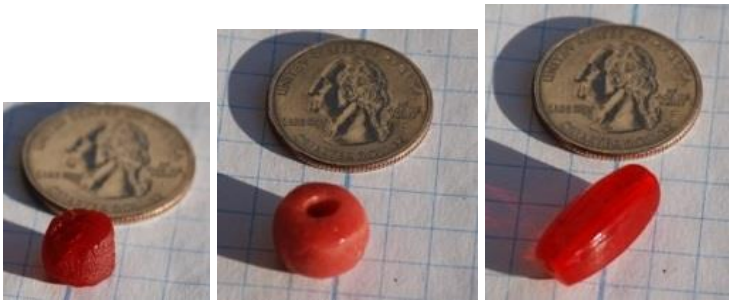


Figure 2.1 i) Red TRGB (left), Red PGB (middle), Red TRGB (right)

Beads were purchased from Cedi Beads Industry, Odumase-Krobo, in the summer of 2012 (left). Beads were purchased from a vendor at the Koforidua Bead Market in the summer of 2014 (middle, right).

Research materials were gathered on two separate trips to Ghana in the summers of 2012 and 2014. This project was initiated by interest in red glass beads obtained from Cedi Bead Factory, in Odumase, Krobo in the summer of 2012 (*Fig. 2.1 i left*). A return trip was organized in the summer of 2014 to interview bead vendors at the Koforidua bead market, the largest in West Africa.

Researchers gained a better understanding of bead-making and marketing in Ghana. On the first excursion to the bead-market, two samples of red beads (PGB and TRGB, respectively) were acquired from an individual (Fig. *2.1*

middle, right): Upon further interview, she confirmed the powdered glass beads were made in Ghana and pointed inquiries to a man who appeared to be a well-known bead-maker in the community.

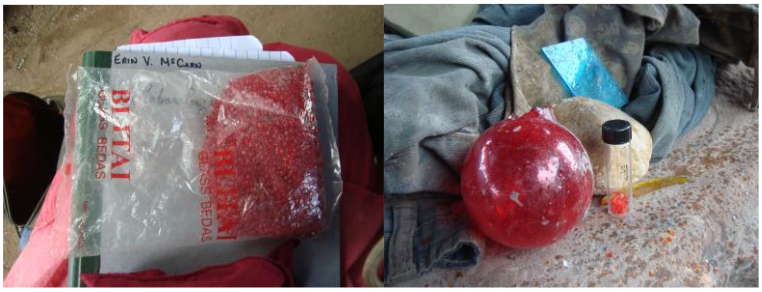


Fig. 2.1 ii) Red TRGB Raw Materials

Obtained from Mr. Alex Oklah Tetteh at Mile 50, Koforidua: Small red glass beads imported from China (Left); rare red glass bottle (Right).

Mr. Alex Oklah Tetteh's contact information was obtained and arrangements were made to meet at his work-shop in Koforidua where two samples of raw materials for red TRGBs (*Fig. 2.1 ii*) were obtained and labeled with numbers corresponding to the date and location of origin. Researchers made and timed the making of red TRGBs; one sample of the finished product was obtained (*Fig. 2.1 iii*). It was in this manner that information was collected from several bead makers in Koforidua and Odumase, Krobo. On a separate visit to the Koforidua bead market, red PGBs were obtained from a different vendor (*Fig. 1.3.1 right*).

Fig. 2.1 iii) Red TRGB in Kaolin-Coated Clay Mold

Made from raw materials in (*Fig. 2.1 ii left*) (Not to scale.)

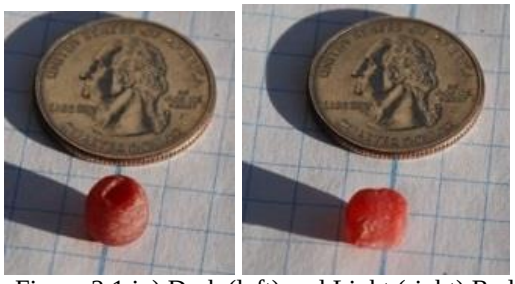


Figure 2.1 iv) Dark (left) and Light (right) Red Over-fired TRGBs

Obtained from Mr. Derick Kpabitey Tetteh; Odumase, Krobo

Two samples of light and dark red over-fired TRGBs (*Fig. 2.1 iv*) and a sample of normal red TRGBs (*Fig. 1.3.2 right*) were collected.

Figure 2.1 v) Light Red Raw Materials for Making TRGB

Obtained from Cedi Beads Industry; Odumase, Krobo; Counterpart to the dark red glass raw materials in (*Fig. 1.3.2 left*).

Interviews were conducted among several workers at Cedi's Bead Factory in Odumase, Krobo, the largest manufacturer of beads in Ghana. A sample of raw red glass dye (*Fig. 1.3.1 left*) was obtained; it was attempted to obtain samples from other bead-makers or the bead market but, these attempts failed due to unavailability or inability to locate the market-stalls. A group of workers was asked to visually separate light (*Fig. 1.3.2 left*) and dark (*Fig. 2.1 vi*) red raw materials, normally mixed together to make TRGBs; samples were obtained.

2.2 Sample Treatment

2.2.1 fragmentation process

A portion of each sample (excluding the raw red dye) was powdered into fine grains at the NC State University Minerals Research Laboratory in Asheville, NC. The samples were not sieved and therefore may contain a variety of granule sizes. The glass samples were placed in identical alumina mortars and manually broken into small fragments with an alumina pestle (Fig. 2.2.1 i). The mortars containing the glass fragments were placed on an automated pulverizing machine (Fig. 2.2.1 ii); the alumina pestles were attached to arms on the machine and lowered into the mortars; the glass was left to grind for approximately half of an hour. The powdered samples were transferred to glass vials and labeled identically to the corresponding "solid" sample vial (Fig 2.2.1 iii).

Figure 2.2.1 i) Alumina Mortar and Pestle Used to Grind Samples

Figure 2.2.1 ii) Automated Pulverizing Machine, NC State University Minerals Research Laboratory in Asheville, NC

Figure 2.2.1 iii) Finely Powdered Glass Beads

2.2.2 chemical digestions

The EPA method utilized in the Quantitative Chemistry Lab Manual was modified to digest the glass samples plus a blank of deionized water for the extraction of heavy and light metals such as cadmium and copper; the blank was subjected to the same conditions as all samples.[27] A hot block was pre-heated to a temperature of 100˚C. According to EDX and PXD data, the raw red glass dye gave an approximate percent by weight of cadmium around 0.5% w/w. Using this information, it was determined an approximate mass of 1 centigram of sample was needed to give a solution with a concentration in the linear range of the AAS. A seven point calibration curve was made for copper and cadmium using 1000.0 μg mL^{-1} AAS grade solutions and dilution schemes according to the linear ranges of the metals. [27] Table 2.2.3b gives instrumental parameters.

The masses of individual beads were taken and a near identical mass (to two significant digits) of the corresponding powdered glass bead was weighed to match the mass of a whole bead. If the beads or glass fragments had a mass below 0.5 grams, more sample was added to reach a minimum mass of 0.5 grams. The samples were deposited into labeled polyethylene digestion vials and using a graduated cylinder, 6.0 mL of 70.4% nitric acid and 3.0 mL of 30.0% hydrogen peroxide were added. The extremely oxidative nature of these reagents increases the concentration of silanols and disrupts ionic interactions at the silica surface through hydrolysis and can dislodge metallic particles from the glass matrix. The digestion vials were placed in the hot-block and the temperature was increased every 10 minutes until a final temperature of 140˚C was reached. The samples stayed on the hot-block until reaching a volume around 2 mL whence they were removed from the hot-block and cooled in the fume hood.

When cooled, 3.0 mL of nitric acid and 1.0 mL of 30.0% H_2O_2 were added. The vials were returned to the hot-block at 140˚C until a volume around 2 mL was reached. This process was repeated thrice to give a total of 4 digestions for each sample with 70.4% HNO_3 and 30.0% H_2O_2. On the fifth digestion, the walls of each vial were rinsed using 5 - 10 mL of 10.0% HNO_3 (aq). 10.0 mL of deionized water and 5.0 mL of 37.2% HCl were added to each vial and returned to the hot-block until a final volume around 10 mL was reached. *During a separate analysis, four 1.0 cg samples of raw red glass dye were analyzed thrice per sample to give a statistically significant value for the Cd content of the dye; the same calibration curve scheme and digestion method was used *excluding* the fifth digestion procedure as light metals had not been detected using PXD and EDX on the raw red glass dye.

Upon AAS analysis, it was determined 9 of the red glass bead samples were too concentrated to fall within the linear absorption range for cadmium and therefore underwent a 3:10 dilution using volumetric glass-ware and deionized water. All systematic error due to glass-ware was accounted for in standard error propagation.

2.2.3 instrumentation and sample preparation

2.2.3a) PXD

A small portion of raw red dye was placed on the glass window of the powder-mount plate using a scoopula and firmly packed. A couple drops of 99% ethanol were dripped onto the sample and allowed to evaporate. The powder-mount plate containing the sample was placed in the sample holder of the X'Pert Philips XRD Empyrean Tube Type: FW3040 – MPD and the spectrum was collected. The data was compared with a library of spectra on the instrument's software. The peaks were compared with characteristic d-values in the crystalline database and peak intensity was used to roughly approximate %w/w compositions. It was attempted to analyze the glass samples using PXD however no useful information was obtained due to glass's non-crystalline character.

2.2.3b) AAS

A Thermo Jarrell Ash Smith-Hieftje 12 aa/ae spectrophotometer with a hollow cathode ray lamp containing the element of interest was used in combination with Beer's Law (Eqn. 1) to calculate appropriate calibration curves in order to determine the %w/w metal content of the samples. Standard error was propagated using the LINEST function in Microsoft Excel 2003.Table 2.2.3 b gives the instrument settings and parameters.

Table 2.2.3b) AAS Instrument Settings[27]

	Copper	Cadmium
Wavelength (nm)	324.7	228.8
Band pass (nm)	1.0	1.0
Lamp Current (mA)	5.0	3.0
High Voltage (V)	380	700
Lower end of linear range (μg/mL)	0.03	0.01
Upper end of linear range (μg/mL)	4.00	2.00
Flame	air-acetylene	air-acetylene

2.2.3c) SEM – EDX

An FEI Quanta 400I D7 903 SEM with an Oxford Instruments INCA X Sight EDX, as seen in Fig. 1.5.2 a, equipped with a tungsten hairpin filament electron source, solid-state back-scatter electron detector (SSD) and an Everhart-Thornley detector (ETD) with a P-type (Li-doped) semiconductor detector, was used to collect EDX spectra and images. In preparation for analysis, powdered samples were mounted using carbon adhesive tabs on labeled aluminum stubs by sprinkling a small amount of sample onto the adhesive-coated stubs. Excess was tapped off. Whole glass bead samples and glass fragments were mounted to aluminum stubs using colloidal graphite in ethanol. All samples were carbon coated using an Ernest F. Fullam Mk II Carbon Coater. Cobalt was used to calibrate the EDX prior to each analysis session.

3. Results and Discussion

3.1 Oral History of Glass Bead-making in the Eastern Region of Ghana

Through collection of oral histories, observation of methodologies, and scientific experimentation, we may gain a greater knowledge of the birth of the blacksmiths, the potters, the glass-makers . . . the scientists born of generational knowledge that regenerate humanity.

3.1.1 Alex Oklah Tetteh (Koforidua)

3.1.1a) history

Mr. Oklah Tetteh explained his business is the culmination of a least a half a century of generational family knowledge; his parents are from Somanya and Odumase, both townships are considered part of the Krobo area within the Eastern Region. They moved to Mile 50, Koforidua before Mr. Tetteh's birth where they continued the family business of bead-making. Mr. Tetteh was exposed to the practice at an early age and recalls aiding in bead-making early on in life.

3.1.1b) methodology

Mr. Tetteh remarked on the rarity and expense of red glass; he went on to say that red glass obtained from broken bottles or stained-glass windows would often change color during the firing process (*Fig 2.1 ii right*). This resulted in unmarketable, opaque beads having a brownish/liver color; as such, he began purchasing small glass beads imported to Ghana from China (*Fig 2.1 ii left*) that did not exhibit such extreme chemical changes upon heating.

Figure 3.1.1b) Kiln at Mr. O. Tetteh's Work-shop, Koforidua

Seen in Fig. 3.1.1 b, the kiln at Mr. Tetteh's workshop was fashioned by digging out a pit for the wood-fueled fire. Cast iron scrap from vehicular breaking systems was laid across the pit to form a platform, on which the glass-containing molds are placed. A dome-shaped structure is formed around the platform using sandy clay taken from Mr. Tetteh's yard. An opening is left in the front of the dome structure for inserting and removing bead-molds. A hole is left open beneath the platform and dome-structure for the purpose of feeding the wood fire and producing a forced draft effect in which more oxygen is pulled into the flame to raise the temperature within the oven.

At Mr. Tetteh's workshop, the red glass star (*Fig. 2.1 iii*) was made according to the following procedure. The empty star mold was immersed in an aqueous solution of kaolin and allowed to dry completely. The mold was then filled with beads seen in (*Fig 2.1 ii left*). It was placed in the kiln for 18 min. 20 sec. at which time it was removed and checked, then returned to the kiln within less than 2 minutes. After 4 min. 35 sec. the star was removed and checked again; it was returned to the oven within less than 1 minute. It remained in the kiln for an additional 4 min. 52 sec. before being removed to cool completely. Immediately after removal from the oven, a metal pike attached to a wooden handle was used to poke a hole in the center of the glass which appeared black; it was surprisingly more viscous than anticipated and a significant amount of force was needed to drive the pike completely through the center. Red color developed slowly during the cooling process. After cooling, the surface of the glass star was smoothed on a concrete slab. The videos taken during this exchange demonstrate how large batches of TRGBs are made after removal from the kiln and made ready for sale by smoothing the beads with sand and water in a concrete slab: (https://www.youtube.com/watch?v=o0dDXIpUOIQ), (https://www.youtube.com/watch?v=Eo8NueDBjnQ).

3.1.2 Derick Kpabitey Tetteh (Odumase, Krobo)

3.1.2a) history

Most bead-makers and vendors spoke clear English; however, a translator was required to facilitate some parts of conversations. Wisdom Dogbey assisted in locating workshops, translating conversations, and aiding in cultural understanding of the bead-makers; interviews with Derick Kpabitey Tetteh required a secondary translator whose name was Samuel. Derick was a much smaller-scale bead-maker and spoke mainly the Krobo dialect of the Dangme language; Samuel spoke mainly Krobo and the Twi dialect of Akan; Wisdom spoke Twi and English. Through these means of communication, information was collected. Mr. Kpabitey Tetteh was born in Odumase, Krobo and has been making beads for at least four years_ his father was a bead maker and his father before him. He confirmed dark red glass to be scarce in comparison to light red glass, complying with the logic that Cd(Se, S) glasses maintain a lighter red, orange hue in comparison to copper and gold glasses which are typically a deeper red with a purplish hue.[15] He went on to say that light red and turquoise blue are the most popular bead colors.

According to Mr. Tetteh, the Krobo peoples came to Ghana from Nigeria due to ethnic wars and brought the trade of bead making with them. This complies with Yoruba migration patterns and archeologically evidenced glass beads from Ife, Nigeria.[8] Mr. Tetteh and his friend, Samuel confirmed bead-making has been present among the Krobo at Odumase for approximately 200 years; they also stated that they heard glass beads are made in the Northern Regions of Ghana from sand and raw constituents. If so, this is an exciting opportunity for future research as little to no literature documentation of this science exists!

3.1.2b) methodology

Figure 3.1.2b) Kiln at Mr. K. Tetteh's Work-shop (Odumase, Krobo)

Unfortunately, Mr. Tetteh was not firing the kiln on the day of visitation. His kiln construction was identical to that described at Mr. Oklah Tetteh's workshop. He also stated he did not have any raw materials for making TRGBs as he had used them all up the day prior.

3.1.3 Nomoda Ebenizer Djaba a.k.a. Cedi, Cedi Beads Industry (Odumase, Krobo)

3.1.3a) history

Mr. Cedi was born in Odumase, Krobo where he inherited the family business and began by making his first beads at the age of seven. He has been making beads for at least 20 years and is president of the Manya Krobo Bead Association; he helped to form the Ghana Bead Society and is a member of the International Society of Glass Bead

Makers. Interviews with Cedi and several employees at Cedi Beads Industry confirmed the Krobo practice of bead-making to date back at least a century; they also verified the Krobos are of Yoruban descent.

3.1.3b) methodology

Cedi Beads Industry uses a mixture of dark and light red sheet glass purchased from an international glass shop in Accra to create TRGBs. Employees stated there was little to no change in glass coloration even with excess heat. They stated that over-fired red PGB would appear pink, having a reaction opposite from what is expected in over-fired TRGBs, providing an excellent topic for future research into the nature raw glass dyes available in Ghana.

Figure 3.1.3b) Kiln at Cedi's Bead Industry, Odumase, Krobo

The kiln construction at Cedi Beads (Fig. 1.3.1b) is identical to the aforementioned kilns with the exception of the sandy clay utilized to construct the dome: They use sand from vacated termite mounds.

The use of termite sand in kiln-construction is unique and worth future research. The hypothesized reasoning is that the termites act as a natural sieve, using smaller granules of sand and their own saliva to build their mounds. This smaller particle size allows for closer packing and thereby, a greater heat refractory index potentially raising kiln temperatures above what can be expected. Mr. Cedi also expressed selectivity in the type of wood used, stating that Mahogany trees are a harder wood and therefore burn hotter.

3.2 Glass Compositions

3.2.1 SEM – EDX

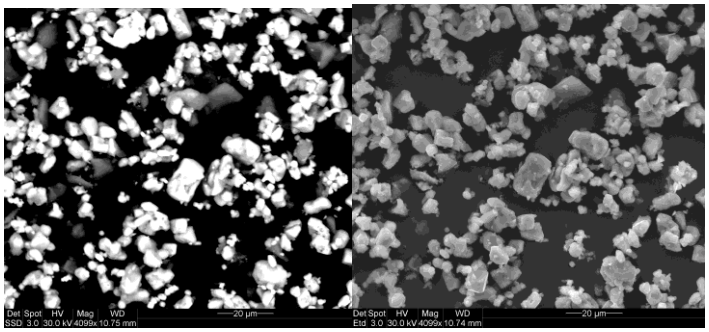


Figure 3.2.1 i) Raw Red Glass Dye

Spot-size = 3.0 nm; Accelerating Voltage (AV) = 30.0 kV; 4099x Magnification; Working Distance (WD) = 10.75 mm (Left, Back-scatter SSD / Right, ETD)

The Everhart Thornley detector of the SEM relies on lower energy secondary electrons produced when the sample is bombarded by high energy electrons. Back scattered electrons are electrons that have struck the sample surface and incurred an almost completely elastic collision; it is good for distinguishing elements of very different atomic numbers.[22] Fig. 3.2.1 i shows images of the raw red glass dye (*Fig 1.3.1 right*) using both detectors with identical instrumental parameters; the ETD is more useful in detecting surface details. All SEM images included from this point were taken using the ETD.

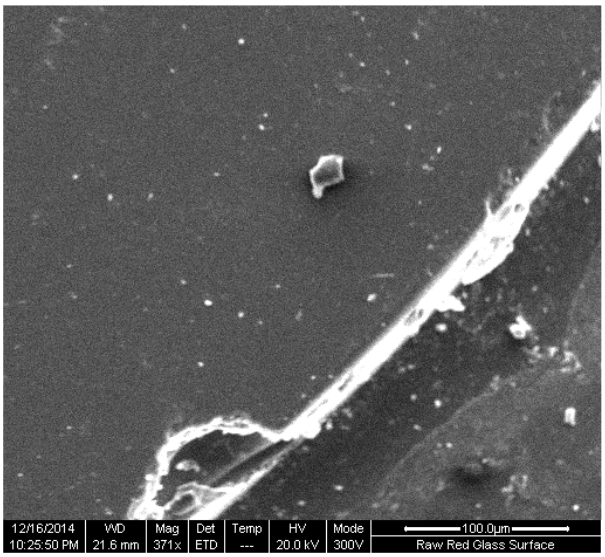


Figure 3.2.1 ii) Translucent Glass Fragments

Unfired red glass fragment from Fig 1.3.2 left. AV = 20.0 kV. WD = 21.6 mm, Mag. = 371x.

Fig. 3.2.1 ii shows a sample of smooth, unfired glass used to make translucent recycled glass beads; this glass had fully reached its melting point before cooling, owing to the homogenous appearance.

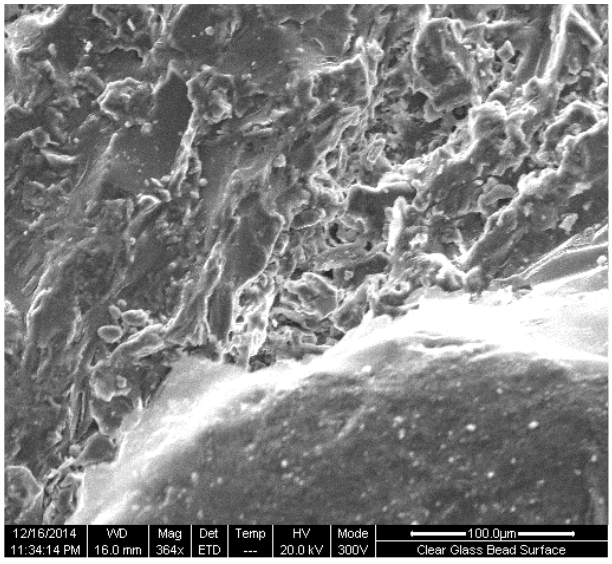


Figure 3.2.1 iii) Red Translucent Recycled Glass Bead

From (*Fig. 2.1 i left*). AV = 20.0 kV, WD = 16.0 mm, Mag. = 364x.

Fig. 3.2.1 iii shows the surface of a red translucent recycled glass bead at about the same magnification of *Fig. 3.2.1 ii*. The translucent recycled glass beads have a craggy, asperous texture, confirming the temperatures in the kiln are not high enough to melt the glass, however at the transition temperature wherein glass becomes rubbery, particles may sinter and agglomerate.

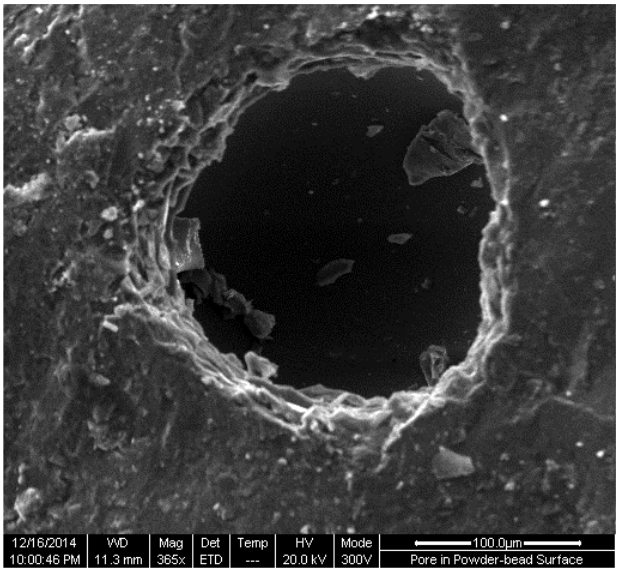
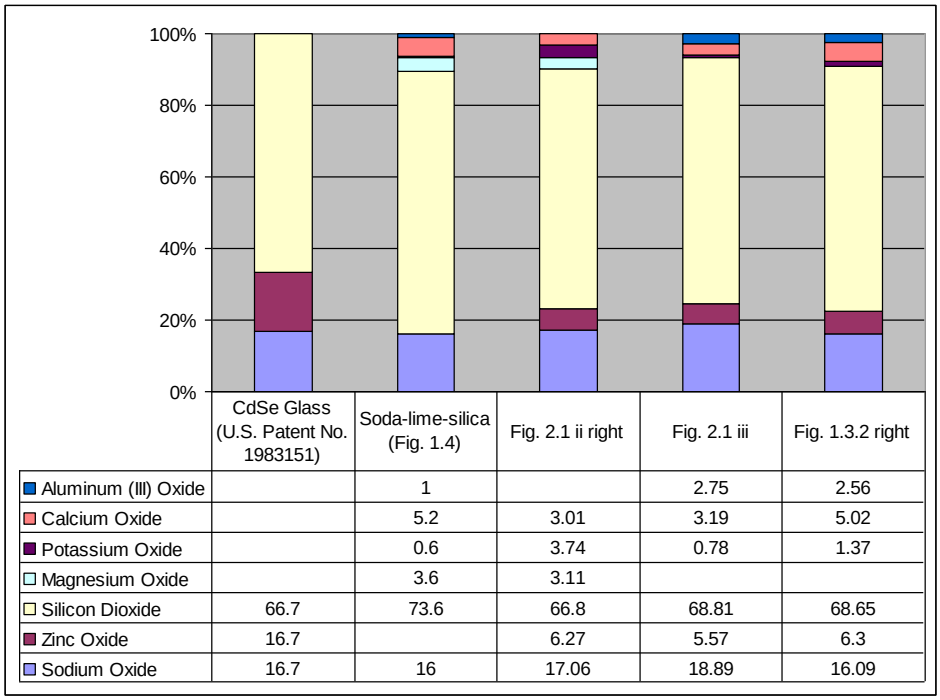


Figure 3.2.1 iv) Red Powdered Glass Bead Surface

From *Fig. 1.3.1 right*. Av = 20.0 kV, WD = 11.3 mm. Mag. = 365x.

Fig. 3.2.1 iv shows a pore at the surface of a red powdered glass bead. The particle size of materials used to make powdered glass beads is less than materials in translucent recycled glass beads. Because the particles have greater surface area, they are able to pack closer together and sintering interactions increase, creating a relatively smooth surface albeit rough in comparison to Fig. 3.2.1 ii. Additional SEM images of a broken powdered glass bead revealed round holes throughout the material. The pitting within the bead's structure is likely due to the agglomeration and escape of air-bubbles during the sintering process.



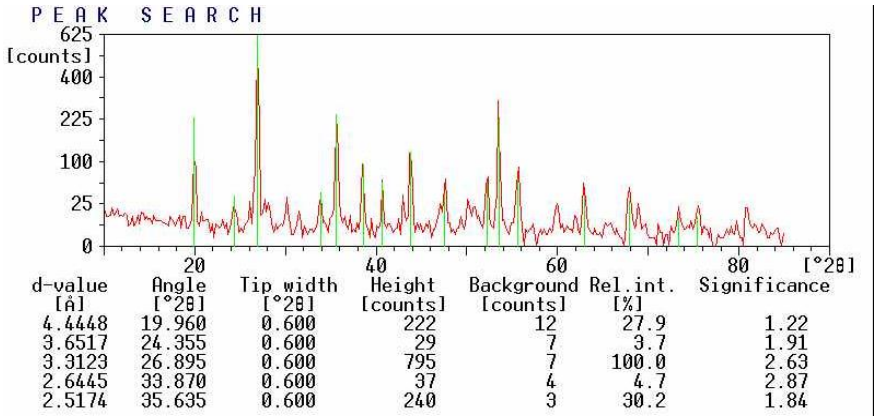
	CdSe Glass (U.S. Patent No. 1983151)	Soda-lime-silica (Fig. 1.4)	Fig. 2.1 ii right	Fig. 2.1 iii	Fig. 1.3.2 right
Aluminum (III) Oxide		1		2.75	2.56
Calcium Oxide		5.2	3.01	3.19	5.02
Potassium Oxide		0.6	3.74	0.78	1.37
Magnesium Oxide		3.6	3.11		
Silicon Dioxide	66.7	73.6	66.8	68.81	68.65
Zinc Oxide	16.7		6.27	5.57	6.3
Sodium Oxide	16.7	16	17.06	18.89	16.09

Figure 3.2.1 v) Compound %w/w comparisons between literature values and experimental values from EDX data

Comparisons between literature values for soda-lime silica glass and industrially manufactured Cd(S,Se) red glass were made with experimental EDX data from several TRGBs. [14, 17]

EDX data affirmed the hypothesis that the beads were made from soda-lime silica glass, with slight variations in composition. It is likely alumina (Al_2O_3) contamination occurred within all samples due to the fragmentation process. U.S. patent No. 1983151 describes the method for commercial production of Cd (S, Se) red glass and gives suggested batch components: Silverman suggests replacing Ca with Zn as a stabilizer, but states the mixture is insensitive to use of traditional stabilizers or reducing agents.[17] All samples included in Fig. 3.2.1 v contain Zn and Ca.

3.2.2 PXD



d-value [Å]	Angle [°2θ]	Tip width [°2θ]	Height [counts]	Background [counts]	Rel.int. [%]	Significance
4.4448	19.960	0.600	222	12	27.9	1.22
3.6517	24.355	0.600	29	7	3.7	1.91
3.3123	26.895	0.600	795	7	100.0	2.63
2.6445	33.870	0.600	37	4	4.7	2.87
2.5174	35.635	0.600	240	3	30.2	1.84

Figure 3.2.2 PXD Spectrum of Raw Red Glass Dye

PXD was utilized to successfully characterize the raw red glass dye obtained from Cedi's Bead Industry (*Fig. 1.3.1 left*). Fig. 3.2.2 shows the spectrum collected and compares the experimental values with literature values for zircon tabulated in Table 3.2.2; the Hanawalt group method allowed for identification of the crystalline solid glass dye. [23, 28] Data from EDX indicated the presence of Cd(S/Se) in the sample, which explains the mixed peaks in the PXD spectrum. The peaks for CdSe roughly match up with spectral peaks but are likely shifted due to a low quantity present. By examining the peak intensity, it can be seen there are roughly 4 parts CdSe per 100 parts $ZrSiO_4$.With these results, it can be concluded the powder is a solid suspension of Cd(S/Se) in zircon.

Table 3.2.2 Literature Values for Zircon [28]

Relative Intensity	d (Angstroms)	2θ	(h,k,l)
100	3.3035	26.99	(2,0,0)
58.11	2.5190	35.64	(1,1,2)
42.36	4.4448	20.02	(1,0,1)

3.2.3 AAS

In an extremely acidic, oxidative environment, the concentration of silanol groups at the silica surface increases as sodium (and probably calcium) ions are stripped away and silicon-oxide bonds are broken down. As the glass matrix breaks down, metallic entities near the glass particles' surfaces are released into solution. It was observed during AAS analysis of finely fragmented glass samples that the flame became remarkably orange-yellow, most likely resulting from the emission spectra of sodium. The flame was observably less orange-yellow when analyzing the "solid" glass samples, indicating the extraction of Na from the glass matrix is dependent on the sample's surface area.

3.2.2a) cadmium

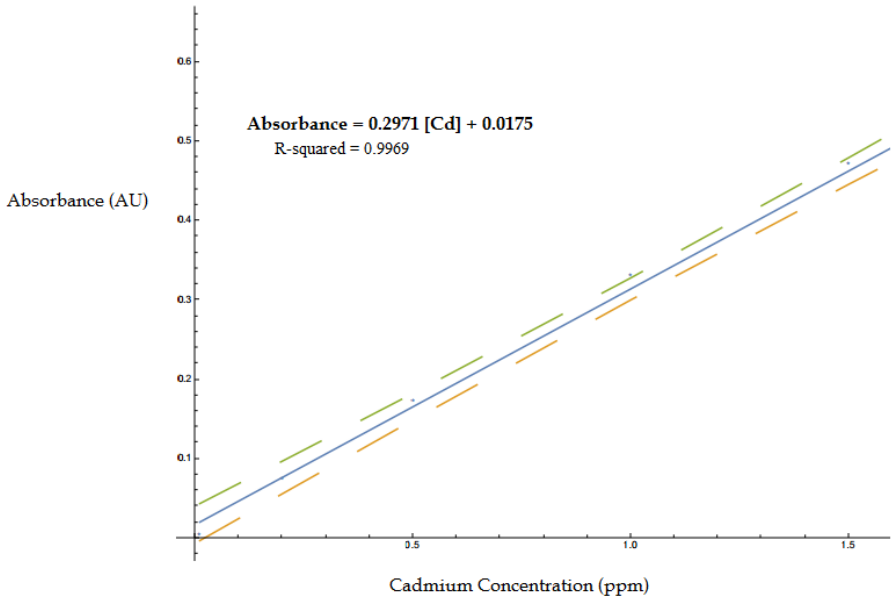


Figure 3.2.2 a i) Cadmium Calibration Curve

Using the Cd calibration curve with error bars shown in Fig 3.2.2a i, the LOD, LOQ, and pap concentration of filtrates were determined from Beer's Law (Eqn. 1) and LINEST data calculated in Excel. Cadmium was present and above the LOQ (0.31 μg mL^{-1}) in all fragmented samples; analysis of whole glass beads yielded results below

the LOD (0.10 μg mL^{-1}) presumably due to the reduced surface areas of the beads in comparison to their fragmented versions. Using concentration with solution volume and the mass of sample, μg mL^{-1} was converted to w/w%. The cadmium concentration of the raw red glass dye (n = 12) was found to have an average % w/w of 0.34 ± 0.01. The cadmium concentration of translucent recycled glass beads widely varied, reflected by the large standard deviation. Table 3.2.2a i gives the complete data for Cd content of red TRGBs.

Table 3.2.2 a i) Cd % w/w of Red Translucent Recycled Glass Beads

Location of Collection	Sample ID	Cd % w/w ± standard deviation	
Alex Oklah Tetteh	Fig. 2.1 iii	0.013	0.009
Derick Kpabitey Tetteh	Fig. 2.1 iv (right)	0.038	0.003
	Fig. 2.1 iv (left)	0.048	0.003
	Fig. 1.3.2 (right)	0.06	0.004
Cedi's Bead Industry	Fig. 2.1 i (left)	0.032	0.002
Koforidua Bead Market	Fig. 2.1 i (right)	0.0057	0.0003
	Average:	**0.03**	**0.02**

The origins of sample ID *Fig. 2.1 i right* are questionable as they did not resemble other TRGBs; it was confirmed beads of this sample fully reached the melting temperature before cooling using SEM. Data for samples *Fig.1.3.2 right* and *Fig. 2.1 i right* underwent statistical Q-tests and, at 99% confidence, are included in the data set. Raw materials used in translucent recycled glass bead creation were analyzed and compared with their finished products, % w/w Cd content of these raw materials are given in Table 3.2.2 a ii.

Table 3.2.2 a ii) Cd % w/w of Red Glass Fragments used in Translucent Recycled Glass Bead Production

Location of Collection	Sample ID	Cd % w/w ± standard deviation	
Alex Oklah Tetteh	2.1 ii (left)	0.035	0.002
	Fig. 2.1 ii (right)	0.021	0.014
Cedi's Bead Industry	Fig. 1.3.2 (left)	0.031	0.002
	Fig. 2.1 v	0.025	0.001
	Average:	**0.028**	**0.006**

A series of T-tests were run at the 99% confidence interval to determine statistically significant relationships between samples. Table 3.2.2a iii gives the results of these T-Tests. Averages of Cd %w/w values were taken for statistical purposes for some samples where indicated in the table. Raw materials *Fig. 1.3.2 left* and *Fig 2.1 vi* were mixed by workers at Cedi's Bead Factory to make beads in *Fig. 2.1 i left*. the sample in *Fig. 2.1 ii left* was used to make sample *Fig. 2.1 iii*. Raw materials and finished red translucent glass beads were found to be statistically identical at 99% confidence.

Table 3.2.2 a iii) T-tests at the 99% Confidence Interval

Samples of Interest	Degrees of Freedom	Calculated T-value (T)	Literature T-value (Tc)	Relationship
Fig. 2.1 ii (left) vs. 2.1 iii [Raw materials vs. finished product]	4	4.13	4.6	T < Tc
Fig. 2.1 iv (left) vs. (right) [Over-fired light red vs. dark red]	4	4.08	4.6	T < Tc
Fig. 1.3.2 (left) & Fig 2.1 vi vs. Fig. 2.1 i (left) [Raw materials vs. finished product]	7	1.51	3.5	T < Tc
Fig. 2.1 iv (left) & (right) vs. Fig.1.3.2 (right) [overfired vs. normal]	7	517	3.5	T >> Tc
Fig. 1.3.2 (left) vs. Fig 2.1 v [dark vs. light red raw materials]	4	4.65	4.6	T > Tc

Samples *Fig 1.3.2 left* and *Fig. 2.1 v* were separated by workers at Cedi's Bead Industry based on a perceived visual difference in hue; they were found to be statistically different at 99% confidence. Samples *Fig. 2.1 iv (left) and (right)* represent beads Mr. Kpabitey Tetteh accidentally kept too long in the kiln: their average % w/w Cd was found to be statistically different from normal beads (*Fig. 1.3.2 right*) produced at the same location. This is most likely due to the surface interactions of CdSe particles with silica described by Masson et al. in which O is replaced by Se under annealing conditions at a minimum temperature of 390˚C, shown in *Fig. 3.2.2a ii*. [29] The Si – Se bond is stronger than the Si – O bond and is indissociable at 140˚C in 3:1 70.4% HNO_3 : 30% H_2O_2 with an added HCl digestion. This mechanism explains why the extractable Cd in over-fired beads is significantly lower than normal beads and offers insight into potential future digestion methods for extraction of colorants from glass matrices.

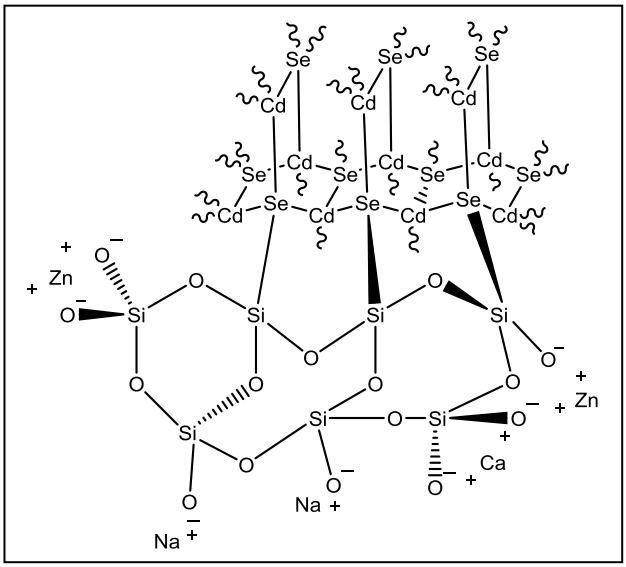


Figure 3.2.2 a ii) Surface Interactions of CdSe and Silica After Exposure to Annealing Temperatures[29]

Continuation of the Cd(S,Se) lattice is implied by the wavy bonds.

Chemical analysis of powdered glass beads yielded results reflecting the observed methods of bead-making: Approximately 1 part dye in 100 parts glass is used. 0.34 parts Cd in the dye compared with 0.004 parts Cd in the glass beads gives a ratio of 1 in 85. The two sample populations of this group were found to have identical Cd %w/w at the 99% confidence interval; the Cd % w/w values are reported in Table 3.2.2 iv. Results were calculated using the same calibration curve and LINEST data as red TRGBs.

Table 3.2.2 a iv) Cd % w/w of Red Powdered Glass Beads

Location of Collection	Sample ID	Cd % w/w ± standard deviation	
Koforidua Bead Market	Fig. 2.1 i (middle)	0.0056	0.0004
	Fig. 1.3.1 i (right)	0.0032	0.0002
	Average:	**0.004**	**0.002**

Given the results obtained in this study, future experimentation would greatly benefit from a greater sample size and variation especially in raw red glass dye(s) and red powdered glass beads. Experimentation with new or different digestion methods may yield more conclusive results; *complete* metal extraction of red dye(s) did not occur with any samples as a visible red hue remained in all solids following filtration.

3.2.2 b) copper

All samples with the exception of *Fig. 1.3.1 i right*, fell below the LOD for copper (0.08 μg mL^{-1}). The "solid"/whole and fragmented samples of *Fig. 1.3.1 i right* gave readings falling below the LOQ (0.24 μg mL^{-1}). It could be worth further testing red PGBs and pure red glass dyes for copper.

4. Conclusions and Future Research

4.1 Conclusions

Ethnochemistry allows researchers to better understand the relationships between chemistry and culture. Further research may yield more conclusive results in determining the origin of Krobo bead-making in Eastern Ghana but ancestral ties with the Yoruba peoples of Western Nigeria appear evident. Presently, it can be concluded the modern sources of red glass in Ghana contain cadmium: All finely fragmented samples contained quantifiable amounts of cadmium. The raw red glass dye in this study is composed of cadmium sulfide/selenide (at least 0.34 ± 0.01 Cd %w/w) suspended in zircon. More samples of raw red glass dye should be collected for future analyses. As evidenced by the sample in *Fig. 1.3.1 i*, copper may be a component in other raw red glass dyes or red PGBs. Testing for chalcogens may yield more results relating to the interactions at the glass – Cd(S, Se) interface in addition to further probing the glasses' accurate percent compositions.

The chemical extraction of cadmium and sodium from glass matrices is dependent on the relative surface area of the glass particles and the sol-gel/ionic nature of the glass surface. If the glass is overheated, Se (and maybe S) in Cd(S, Se) replaces O at the Si – O matrix surface, barring some Cd from extraction using the digestion method in this study. It can be concluded with 99% confidence that: no chemical changes occur in the colorants of red TRGBs when properly fired; the Cd content of dark and light red glasses are statistically different, but further testing could prove otherwise. In PGB, the extraction method was relatively successful as evidenced by the calculated ratio of 1 part Cd to 85 parts clear glass coincides with the experimentally observed ratio of 1 part dye to about 100 parts powdered clear glass.

4.2 Future Research

Return trips to Ghana are necessary in order to collect more oral histories and materials, especially raw red glass dye and red powdered glass beads. Determination of the mechanism of decoloration in over-fired PGB poses an interesting route to developing new red glass colorants. Other colors/colorants are interesting topics for research as well. Measuring the heat refractory index of kiln construction materials, the temperatures within the kilns during firing, and making detailed observations on kiln construction in relation to geographic and ethnic identities will contribute significantly to understanding the history of material development in West Africa. Excursions into the Northern Regions of Ghana could produce exciting new insight into the practice of glass-making from entirely raw materials like chalk, potash or soda ash, and sand!

EDX analysis of all samples needs to be completed. Modifications to well known digestion methods may yield better results. The fragmentation procedure could be modified to produce smaller, more uniform particle sizes that would better undergo extraction as evidenced by the extreme dependence on sample-particle surface area. Modification of procedure could yield more conclusive results in regards to the Cu content of samples like in Fig. 1.3.1 i or achieve near complete metal extraction from glass samples. Revisiting the UV/Vis and modifying analysis procedures could produce better results. Other spectroscopic methods like Mössbauer could yield useful results.

5. Acknowledgements

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- Mr. Wisdom Dogbey – My partner who helped navigate us through the Eastern Region of Ghana and translate cultural and conversational lessons. Thank you.

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