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**Gold Nanoparticle Colorants as Traditional Ceramic Glaze Alternatives<sup>†</sup>**

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**ABSTRACT**

Historically, Roman stained glass has been a standard for high temperature color stability since biblical times but was not properly characterized as emission from nanoparticle plasmon resonance until the 1990's. The methods under which it was created have been lost, but some efforts have recently been made to recreate these properties using gold nanoparticle inks on glassy surfaces. This body of work employs gold nanoparticle systems ranging from 0.015 – 0.100 % (wt/wt) suspended in a clear glaze body. The glazes are fired with traditional ceramic methods – in both gas reduction and electric oxidation kilns – in which nanoparticles are retained and can be imaged via TEM. Various colors intensities are reported in addition to changes in nanoparticle size after application and firing. The nanoparticle glazes are compared to traditional red glazes, highlighting the significantly lower metal loading required (5-10% for traditional glazes vs 0.100 % for gold (wt/wt)), therein. Finally, proof of concept is provided with a functional gold nanoparticle mug, fired in reduction, that costs roughly 0.98\$ USD in gold used.

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<sup>†</sup> Patent pending.

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## 1. Introduction

The use of metal nanoparticle (NP) color alternatives allows for a metal-efficient and ecologically advantageous route to high-temperature permanent color on glass, silica surfaces, and in feldspathic ceramic glazes.<sup>1,2</sup> This color is achieved through surface plasmon resonance (SPR) emission and has been demonstrated to be dependent on NP diameter, shape, and concentration for both intensity and wavelength of color.<sup>3,4</sup> SPR emission is dependent on charge-density oscillations of individual particles and aspect ratio of non-spherical structures, which allows for color tuning despite being trapped in a solid glaze melt or silicate matrix.<sup>5,6</sup> To that end, a variety of colors and shades (intensities) can be achieved by tuning NP diameter, aspect ratio, concentration of NP, and through controlling the methods by which these feldspar/silicate ceramic coatings are cured.<sup>5</sup> These noble metal NP have been observed in ancient Roman works<sup>7,8</sup> to Middle Age and Renaissance art<sup>9,10</sup> as stable and oxidation-resistant color sources where organic chromophores decompose over time and do not survive ceramic or glass curing processes.<sup>11</sup> The inkjet printing of metal NPs to ceramic surfaces has recently been demonstrated but the technology has yet to be adapted to bulk glaze materials for commercial ceramics.<sup>12,13</sup> The use of noble metal NPs in glazes would allow for effective coloring with low total metal loading concentrations that minimize leaching and avoid the heavy metal toxicity of traditional glazes.

Currently, modern approaches to developing nanomaterial color in ceramic glazes include the application of metal salts and then nucleation and growth within the silicate/feldspar glaze<sup>2</sup> and the application of gold nanoparticles (AuNP) to a ceramic surface via inkjet printing followed by silicate/feldspar ceramic glaze over the AuNP ink,<sup>2,14</sup> both of which have demonstrated stability up to traditional cone 10 firing temperatures – 2345 °F (1200 °C). These are performed in controlled lab settings, with precise equipment and firing schedules; they have not been developed for current commercial use and broad scale studio application, to be fired alongside pottery in traditional kilns and atmospheres. Unfortunately, the cost of gold is currently inhibitive of full adoption of this technique by commercial pottery standards; however, this work can allow for the eventual replacement of more traditional toxic metal colorants in functional ceramic surfaces, including cobalt, barium, manganese, nickel, and chromium.<sup>15</sup> These toxic metals are still standards in pottery glazes for desirable colors, despite difficulties with leaching from ceramic glaze surfaces.<sup>16</sup> Additionally, this technology has not been adapted to commercial or traditional reduction firing techniques, including traditional pottery firing schedules in a reduction gas kiln. To that end, the development of various Au and other metal NP color alternatives in traditional ceramic glazes is a step toward lowered ecological mining impact, lowered toxic metal exposure during pottery use, and lowered net metal glaze colorant and thus cost.<sup>17</sup> Specifically, the use of Au NPs for ceramic glazes represents a strategy with relatively innocuous toxicity risks given the nanomaterial has been established as safe for human cells<sup>18</sup> and is currently used in the medical field as a radiological contrast agent<sup>19</sup> and in

cancer diagnosis/therapy.<sup>20</sup> Additionally, in the event of metal leaching from a ceramic vessel used for consumption, elemental or ionic gold poses a significantly lower toxicity than other metals used in traditional glazes, including Pb, Cd, Ni, Cr, and Mn.<sup>21</sup>

In this paper, a red, gold nanoparticle glaze is prepared with traditional firing methods with and without tin oxide opacifier in addition to various traditional, reduction-fired red glazes; the traditional glaze metal loading requirements for color are listed, such that relative toxicity, environmental impact, and cost are emphasized for comparison. Additionally, the stark contrast between traditional colored glazes and their metal loading verses the metal loading observed for red nanoparticle color glazes is highlighted. Retention of NP color was pursued, with opacifier addition and corresponding effects on color intensity. Contrasting milligram and microgram metal usage in nanomaterial systems, traditional ceramics have significant room for improvement in glaze profile, metal loading, and reduction of opacifier use, which ultimately requires color to be solely dependent on bulk metal at the glaze surface. The technologies presented herein represent significant advancements and allow for the replacement of commercial ceramic colorant methods, while retaining the costly equipment and firing methods already used.

## 2. Experimental Details

### 2.1 Materials.

All chemicals were purchased from Sigma-Aldrich excluding raw glaze materials. All solutions were prepared utilizing 18.3 M $\Omega$ -cm ultra-purified water (UP H<sub>2</sub>O). All raw glaze materials are bulk industry standards and were purchased from ClayWorks in Richmond, VA.

### 2.2. Synthesis of nanoparticles, formulation of glazes, firing of test tiles

Citrate-stabilized nanoparticles (CS-NPs) were synthesized from in-house HAuCl<sub>4</sub> using the procedures developed by Natan and co-workers.<sup>22,23</sup> Briefly, a 1 mM HAuCl<sub>4</sub> aqueous solution was placed in a flask fitted with a reflux condenser and brought to reflux with constant stirring. Ten milliliters of a 38.8 mM (aq) sodium citrate solution was added and promoted color transitions from light yellow to colorless and to burgundy (wine red) were observed. After 10 min of reflux, the solution was removed from heat and allowed to cool to room temperature with continued stirring. The product was vacuum filtrated with a 0.8  $\mu$ m Gelman membrane filter and stored protected from light. Characterization of CS-NPs by UV-Vis spectroscopy (Agilent 8453 Photo Diode Array) and transmission electron microscopy (TEM) showed the characteristic surface plasmon band (SPB) at 520 nm ( $\lambda_{\text{max}}$ ) and an average diameter of 13.9  $\pm$  1.2 nm (**Figure 1**). *Note: Glassware for synthesis of CS-NP must be extremely clean and aqua-regia treatment of all*

*glassware is recommended.* **WARNING:** Aqua regia is a 3:1 ratio of concentrated HCl:HNO<sub>3</sub> and is extremely dangerous making personal protected equipment essential.

Clay sample tiles were prepared from a purchased, commercially available clay, which is a stoneware-porcelain blend and is considered vitrified at cone 6 (2200 °F or 1200 °C) and is stable at cone 10 (2345 °F or 1285 °C). A white surface was needed, since color was to be determined with both translucent glaze formulas and with added opacifiers.

### 2.3 Red glaze standard materials

As a comparison, the following red glazes were also prepared and fired onto glaze tiles, including Panama Red, Tomato Red, Oxidation Raspberry, and Pete's Cranberry, **Figure 2 (a-d)**, respectively, with recipes that include colorant details and metal-loading amounts. The original citrate-stabilized Au NPs were concentrated in an SORVALL RC-5B ultracentrifuge at 10,000 rpm at 5 °C for 1.5 hours. The supernatant solution was poured off and the resulting concentrated NP solution was collected as roughly 30 mL for each batch. For preparation of the AuNP-loaded glaze, a dry glaze powder was prepared in 80 gram batches of 20% G200 feldspar, 20% Ferro Frit 3134, 20% EPK, 19% flint/silica, 15% wollastonite, and 6% talc - all weight-by-weight percentages (wt/wt). The concentrated Au NP was added to each glaze mixture in volumes allowing for 0.015 %, 0.050 %, and 0.100 % loading (wt/wt), water added as needed, mixed, sieved, and applied to tiles. Additionally, the use of an additional 4% tin oxide, SnO<sub>2</sub> (wt/wt), was included against all neat glazes, as tin(II)oxide is a known getter reductant and tin(IV) oxide is a color brightener/attenuator in modern glaze formulation.<sup>24</sup>

For oxidation atmosphere samples, tiles were loaded in electric nichrome coil kilns at the Visual Arts Center of Richmond and fired on a medium temperature ramp in an oxygen-rich atmosphere. It should be noted that these kilns are not vented via a large hood and air/fume convection, but have a fan/draw system that pulls air down, through the kiln and out a port in the base of the kiln, which contributes to an increased oxidative atmosphere during firing. As a test, a glaze with Cu<sub>2</sub>O red copper was prepared, fired in this atmosphere, and was observed to turn green (oxidation state change from Cu<sup>2+</sup> to Cu<sup>3+</sup>) due to the oxidative nature of this process.

For the reduction atmosphere firing samples, tiles were loaded in a sliding door gas kiln alongside normal student pottery at the Visual Arts Center of Richmond. Pilot lights were started immediately after loading to slowly warm the brick kiln and the chimney, such that air draw would be initiated. After roughly 4 hours of pilot light heat, burners were started on a very low setting, left on overnight, and slowly heated the kiln to roughly 800-1000 °F (427-538 °C) by the next morning with a slightly reductive atmosphere via CO production via natural gas combustion.<sup>25,26</sup> The next morning, burners were put on 2 pounds of gas pressure, such that the kiln is put into a soft reduction climb and monitored. Upon reaching cone 012, ~1640

°F ( 893 °C), gas pressure is increased to 3 pounds and the chimney damper is pushed in slightly, limiting the amount of oxygen access to the combustion process and thus creating an aggressively reductive atmosphere in the kiln. This change is visible by a significant difference in flame color (red-orange), soft movement of flame inside the kiln, and by soot production. This atmosphere is maintained up to roughly cone 04, ~1940 °F (1060 °C), after which a softer reduction atmosphere is created by allowing increased chimney air flow. This softer reductive atmosphere is maintained for the remainder of the firing to cone 10, 2345 °F (1285 °C), after which the gas is shut off, all ports are closed, and the kiln is allowed to cool slowly over 36 hours to prevent cracking/crazing/dunting of the ceramic surfaces. It should be noted that other methods that demonstrated some form of nanomaterial color create and fire a clear glaze and then print nanoparticle ‘inks’ on the surface, with a third firing to cure those nanomaterial ‘inks’.<sup>1,2,27</sup>

## 2.4 Characterization of materials

Fired glaze tiles were collected and small glaze samples were processed in a mortar/pestle for roughly one minute before being suspended in ethanol and deposited on copper 400-mesh TEM grids. Images of glaze tiles were obtained for each set of samples in reduction and oxidation at 0.015 %, 0.050 %, and 0.100 % AuNP both with and without 4% SnO<sub>2</sub> opacifier (wt/wt). HR-TEM imaging of the tiles was performed, which was somewhat challenging. The glaze exists as a silicate matrix with the gold nanoparticles locked in a solid suspension and distributed throughout. TEM imaging analysis of the samples showed large silicate glaze grains with AuNP initially visible at the edge of grains. In these, imaging of the particles was performed by focusing down, through cross-sections of grains, in which some few gold nanoparticles are in focus and others are blurred dependent on the depth of focus into the grain and the depth of each respective particle in relation to that focus. Multiple images were taken of each sample at 80 kV, 50,000x magnification, such that roughly 100 particles could be used for sizing analysis and histogram generation. Spectroscopic measurements were conducted with a UV-Vis photodiode array spectrophotometer (Agilent 8453) for solutions and a spectrophotometer with a reflectance sample holder (Varian Cary 5000) for solid ceramic samples. A graphite furnace atomic absorption spectrophotometer (Varian GTA120AA240Z) was used to assess gold leaching from ceramic vessels.

## 2.5 Application of metal colorants in ceramic glazes

Traditionally, specific heavy metals allow for various vibrant colors over time and under extreme conditions. These systems are either opaque or translucent, which calls for various metal loading amounts. If a glaze is translucent, light must pass through it, strike metal colorants in its path, hit a white clay body, and be reflected back out, again striking more metal colorants to produce a visible color. This allows for vibrant, jewel-like colors. With opacifiers and thus opaque glazes, a rather large degree of metal – upward

of 8-fold the amount needed for translucent glazes – is required at the metal surface, as light does not penetrate and reflect off of a white clay surface. While this will make a glaze more versatile to various clays, it also greatly increases cost, creates greater exposure hazards, and is more environmentally taxing with respect to opacifier and bulk metal consumption.

### 3. Results and Discussion

#### 3.1 Preparation and stability of AuNP Glaze

Prior to incorporation into the glaze base, it should be noted that these nanoparticle systems are notorious for aggregation after 2-3 weeks, as citrate is a weaker passivant compared to thiol-capped NPs, for example, that exhibit stability for weeks to months.<sup>28</sup> Within two weeks of being prepared, nanoparticle samples were collected, processed as described above (Figure 1), mixed into glaze bases, applied to ceramic test tiles, and fired in various reduction/oxidation methods. Upon being fired, gold nanoparticle presence appears to be retained more in reduction-fired methods, as a red-purple color is visible in samples ranging from 0.015% - 0.100% Au loading (wt/wt) in both neat and 4% SnO<sub>2</sub> opacified samples (**Figures 3 and 4**, below). Reflectance spectroscopy of these materials (Supplemental Materials, Figure S3) reveals the presence of a surface plasmon band (SPB) with a  $\lambda_{\text{max}}$  between 550-560 nm, a spectroscopy signature attributed to AuNPs (Fig. 1) and notably absent in blank measurements at unglazed ceramic. Of note in the oxidized samples, there is a significant difference in color compared to the glazes from the reductive environment, but a faint red color is retained in 0.050% and 0.100% (wt/wt) AuNP samples. The phenomenon of a reductive environment acting to stabilize nanoparticles is well-established for producing nanoparticles in solution as most syntheses proceed through a nucleation-growth transition in the presence of a reductant such as citrate, as used here for citrate-stabilized nanoparticles (Fig. 1)<sup>23</sup>, to stronger reductants like sodium borohydride, commonly employed in the Brust reaction to form thiol-capped or monolayer-protected gold clusters.<sup>29</sup> The distinctive coloring of the nanoparticle-infused glazes that emerge from the reductive environment in Figures 3 and 4 suggest that the reductive kiln environment is having a similar effect. Reductive kilns, manipulated via the damper and air controls to burn natural gas with low oxygen content, cause incomplete combustion and the formation of carbon monoxide. The carbon-monoxide strikes the ceramic being fired, extracting oxygen content at the interface, and creating an electron rich environment at the surface capable of reducing the oxidation state of metals.<sup>28</sup> In contrast to the red glazes produced in the reductive kiln, oxidative environments in oxygen rich, electric kilns result in oxidation of metal species (Supplemental Materials, Figure S1) and, in the case of nanoparticle doping, significantly less distinctive color (Supplemental Materials, Figure S2).

### 3.2 Nanoparticle characterization

TEM analysis was performed on the glazed ceramics, yielding sample images for all glazes from oxidation and reduction environments. Visible in **Figure 3**, gold nanoparticles are observable at the lowest gold salt loading reduction sample, 0.015 %, with consistent particle sizing analysis through the 0.050 % and 0.100 % Au salt tiles (wt/wt). For the reduced neat tiles, gold nanoparticles were imaged with average particle diameters of  $4.7 \pm 0.7$  nm,  $5.5 \pm 1.4$  nm, and  $5.0 \pm 0.6$  nm for the 0.015%, 0.050%, and 0.100% (wt/wt) Au samples, respectively. For the oxidized neat tiles, particle sizing revealed diameters of  $5.2 \pm 0.7$  nm,  $4.2 \pm 0.7$  nm, and  $5.2 \pm 1.0$  nm for the 0.015%, 0.050%, and 0.100% (wt/wt) Au samples, respectively. Interestingly, these diameters are statistically similar across reduction and oxidation atmosphere firings, despite drastic differences in atmosphere and visible color. Additionally, it is significant that the gold nanoparticles have reduced in diameter roughly by half in the process of firing, both in oxidation and reduction atmospheres. In **Figure 4**, below, similar trends were observed in particle size across oxidative and reductive firing methods for both systems with 4% (wt/wt) SnO<sub>2</sub> opacifier. For the reduced tiles with 4% SnO<sub>2</sub>(wt/wt), gold nanoparticles were imaged with average particle diameters of  $5.2 \pm 0.7$  nm,  $4.4 \pm 0.7$  nm, and  $4.7 \pm 0.3$  nm for the 0.015%, 0.050%, and 0.100% Au (wt/wt) samples, respectively. For the oxidized samples with 4% SnO<sub>2</sub>, particle sizing analysis revealed diameters of  $5.2 \pm 0.7$  nm,  $4.1 \pm 0.6$  nm, and  $5.2 \pm 0.9$  nm for the 0.015%, 0.050%, and 0.100% Au (wt/wt) samples, respectively. Again, all particle diameters are statistically similar, which is surprising considering the visible differences in the samples and the dichotomy of firing conditions. It is thought that the brightness and depth of color is a function of particle concentration, a parameter difficult to assess with the sampling capability of TEM. This hypothesis is supported by the reflectance spectroscopy of the samples (Supplemental Materials, Figure S4) where the intensity of the SPB is clearly dissipated for the glaze from the oxidative firing environment compared to that from the reductive environments. This result suggests that the red coloring is consistent with sufficiently high concentrations of AuNPs within the glazes.

Regardless of the nature of the environment, TEM analysis of the glazes after firing indicates that the diameter of the nanoparticles are significantly decreased (Fig. 3 and 4), some by more than 50%, from the starting nanoparticle material. The exact reason for this decrease is unclear and warrants further investigation. It may be that the kiln environments partially erode the nanoparticles within the glaze during firing. Another hypothesis is that the nanoparticles decompose completely from heating and enter a new, additional nucleation-growth cycle during the firing process. These studies are non-trivial and are currently being undertaken in our laboratory.



### 3.3 Color performance of ceramic glazes

In traditional red glazes, SnO<sub>2</sub> is used as a bulk opacifier, but it is also a coordination environment modifier that affects the D-orbital splitting of other metal colorants, notorious for reds appearing significantly brighter.<sup>24</sup> These effects are most common for copper and chromium. In addition to an oxidation/reduction comparison, 4% SnO<sub>2</sub> (wt/wt) tiles were made (**Figure 4**), and some slight brightening was observed with gold salt across reduction-fired samples, highlighted by a brighter red patch in the 0.100% (wt/wt) Au reduction tile; however, this is negligible compared to copper and chromium color-shifting effects. For reduced samples, color is immediately visible at 0.015% (wt/wt) Au loading and intensifies up to and through 0.100% (wt/wt) Au. This is true for both the neat and opacified samples fired in a reduction atmosphere. For the oxidation tiles, no red color is visible at the lowest loading while a faint pink color becomes visible at 0.050% AuNP and retains a roughly consistent red intensity at 0.100% (wt/wt). For the reduction atmosphere glaze samples, TEM analysis revealed stable gold nanoparticles suspended within the glaze. In the base glaze recipe, no other metal colorant was included; additionally, the original glaze is a clear base, adapted from the University of Miami Ceramics Department via Ron Roy. This presence of color and imaging of AuNP supports the presence and majority contributor of color from plasmon resonance of the gold nanoparticles. Surprisingly, the faint pink color of the oxidation-fired samples is likely due to plasmon resonance as well, as the particles can be imaged via TEM and are statistically similar in size. Visible in **Figure 4**, above, color trends are similar for the opacified samples as that of the neat samples between reduction and oxidation-fired tiles. No significant brightening was observed in the oxidation tiles, though opacity was noticeable alongside a pink/faint red tint. Again, all samples possessed gold nanoparticles, imaged via TEM analysis, which possessed statistically similar size distributions.

Additionally, the NP-doped glaze material can be both dipped and spray-applied to ceramic surfaces, fired under traditional reduction methods, and create functional, low metal-loading wares, as seen in **Figure 5**. At 39 mg of HAuCl<sub>4</sub> per 100 mL batch of colloidal AuNP, this mug contains (at most, after centrifugation) 23 mg Au metal for color. With the current market rate of gold at 1,214\$/ounce, this mug costs roughly 0.98\$ USD in gold.

A leaching study was conducted to help confirm that these new AuNP glazes represent a safer, more environmentally friendly alternative to coloring ceramics. The established protocol for leaching in ceramic materials involves exposure of the product to 5% acetic acid (pH 3) over an extended amount of time.<sup>30,31</sup> The study was conducted by exposing AuNP glazed mugs (Fig. 5) to the extraction solution both with and without microwave heating to simulate usage over the course of 8 days (192 hours), representing aggressive leaching conditions. During this time, aliquots of solution periodically removed from the mugs were tested for the presence of a SPB and gold content via UV-Vis spectroscopy or graphite furnace atomic absorption spectroscopy, respectively. No evidence of a SPB was found after 192 hours of exposure

(Supplemental Materials, Figure S5) and the gold content in solution from both mugs was indifferent from the blank measurement, signifying an undetectable (at ppb) level of gold present in the solution (Supplemental Materials, Figure S6 and Table S1).

### **3.4 Comparison of glaze recipes and metal colorant loading**

Compared to traditional red glazes (**Fig. 2**) with metal oxide colorants and coordination environment brighteners/opacifiers ranging from 2 to 11% (wt/wt) -- the use of nanoparticles for low metal loading color alternatives through plasmon resonance allows for comparable color systems with anywhere from 20 to nearly 1000 fold less bulk metal loading. These colors and surfaces are comparable to current systems that wastefully use bulk metal at the glaze surface. With color appearance at 0.015% (wt/wt) Au and stable, hearty color present at 0.100% (wt/wt) Au, this work presents a new color alternative that is both ecologically and environmental advantageous.

## **4. Conclusions**

While a few novel technologies exist in which a third firing is necessary for the nanoparticle application on the surface of an already formed/fired glaze, this body of work represents stability in a second, standard reduction glaze firing. With color systems visible at 0.015% metal loading (wt/wt) without a coordination environment attenuator and opacifier, new colors with less ecological impact are not only viable, but realistic within the next decade, as these systems are applicable to current firing methods and practices. With fine tuning, these plasmon resonance-colored silicate systems can replace current technology and diminish the cost of metal mining, the ecological impact of such endeavors, and produce surfaces with less metal-toxic leaching concerns. While this work is incredibly exciting, it is still not fully understood. Studies are currently in progress to elucidate the mechanism responsible for a reduction in particle size, both in reductive and oxidative firing atmospheres, in addition to differences in visible color as a function of those conditions.

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## Captions

**Figure 1.** Characterization of citrate-stabilized gold nanoparticles (CS-NPs) including (A) transmission electron microscope imaging (80 kV; 50,000x magnification) and (B) UV-Vis spectroscopy. **Insets:** (*upper*) TEM image (80 kV; 120,000x magnification) and (*lower*) histogram analysis of CS-NPs with average core diameter estimated at  $13.9 \pm 1.2$  nm ( $n = 80$ ).

**Figure 2.** Common red glazes in traditional ceramics, both in oxidative and reductive atmospheres **a-d**, and an example of the nanoparticle red glaze, **e**. Under each is the corresponding recipe, with emphasis on colorant/opacifier loading.

**Figure 3.** Neat samples of AuNP glazes without SnO<sub>2</sub> opacifier, ranging from 0.015% (wt/wt) AuNP loading to 0.100% (wt/wt) AuNP loading (*top-to-bottom*). Samples were fired in both reduction and oxidation atmospheres (*left and right, respectively, in both the photographs and TEM images*). All particle sizes are statistically similar.

**Figure 4.** Opacified samples of AuNP-impregnated glazes with 4% (wt/wt) SnO<sub>2</sub> are shown above, ranging from 0.015% (wt/wt) AuNP loading to 0.100% (wt/wt) AuNP loading (*top-to-bottom*). Samples were fired in both reduction and oxidation atmospheres (*left and right, respectively, in both the photographs and TEM images*). All particle sizes were observed to be statistically similar.

**Figure 5.** A single mug, 0.050% (wt/wt) AuNP, fired in reduction alongside other student pottery at the Visual Arts Center of Richmond.