

# **The Effects of Colorant Oxides and Firing Rate on the Nucleation and Growth of Zinc Silicate Crystals in Crystalline Glazes**

Nicolas Coffey  
Materials Engineering Department  
California Polytechnic State University, San Luis Obispo  
Advised by Dr. Katherine C. Chen

# Approval Page

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Author: Nicolas Coffey

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CAL POLY STATE UNIVERSITY  
Materials Engineering Department

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Prof. Katherine C. Chen  
Faculty Advisor

\_\_\_\_\_  
Signature

Prof. Trevor Harding  
Department Chair

\_\_\_\_\_  
Signature

# Abstract

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This study looked at the effects of colorant oxides and firing rate on the nucleation and growth of crystals in zinc-based crystalline glazes. One weight percent of iron and copper oxide powders were mixed separately with a zinc-based crystalline glaze. The uncolored glaze along with both colored glazes were applied to test tiles and fired. Two different firing schedules were used with different ramp up firing rates of 165°C/hr (slow) and 205°C/hr (fast). X-ray diffraction (XRD) analysis found both zinc oxide and silica oxide in the raw glaze, which are the main components in the formation of zinc silicate. XRD analysis of the fired glaze found zinc silicate, the main component of the crystals. XRD analysis was unable to pick up traces of either the copper or iron oxide. X-ray florescence was used to check for oxide concentration in the glaze. 0.59% Cu was found in the copper oxide glaze while 0.92% Fe was found in the iron oxide glaze. The number of nuclei were counted using the assistance of computer software. The size of the crystals was calculated using the intercept method to get a grain size value for the crystals. The addition of copper oxide and iron oxide decreased the number of nuclei by an average of 60.2% and 84.0% respectively. It also reduced the grain size number of the crystals by 35.5% for the copper and 38.5% for the iron. The change from the slower firing rate to the faster firing rate decreased the number of crystals in the uncolored glaze by 43.8% and decreased the average number of crystals in the copper oxide and iron oxide glazes by 76.1% and 61.0% respectively. The crystal sizes were also reduced by 22.8% for the copper, 27.0% for the iron and 18.8% for the uncolored glaze on average. The results of this study showed that the addition of colorant oxides or increasing the ramp up rate produced less crystals which were larger in size.

Keywords: materials engineering, crystalline glazes, zinc silicate, ceramic glaze, nucleation, growth, firing rate, crystals

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# Table of Contents

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<b>Introduction</b>	7
<b>Broader Impacts</b>	7
<b>Background</b>	8
<b>Crystalline Glazes</b>	8
Basic Composition	8
Other Additives	8
Crystal Formation	9
Firing Schedule	10
Common Problems	10
<b>Factors Affecting Growth of Crystals</b>	11
Glaze Composition	12
Firing Schedule	12
Other Factors	13
<b>Experimental Procedures</b>	14
<b>Sample Preparation</b>	14
Clay Tiles	14
Glazing	14
Firing	15
<b>Data Collection</b>	16
Number of Crystal Nuclei	16
Crystal Size	16
X-Ray Diffraction (XRD)	16
X-Ray Florescence (XRF)	17
<b>Results</b>	17
<b>Crystal Shape and Color</b>	17
<b>Crystal Nuclei</b>	18
<b>Crystal Size</b>	19
<b>X-Ray Diffraction (XRD)</b>	20
Unfired Tiles	20
Fired Tiles	21
Additional XRD Scans	21
<b>X-Ray Florescence (XRF)</b>	22
Uncolored	22
Copper Oxide	22
Iron Oxide	22
<b>Discussion</b>	23
<b>Crystal Shape and Color</b>	23
<b>Number of Nuclei</b>	24
<b>Crystal Size</b>	24
<b>X-Ray Diffraction (XRD)</b>	25
<b>X-Ray Florescence (XRF)</b>	25
<b>Conclusions</b>	26
<b>References</b>	27

# List of Tables

---

Table I: Preprogrammed Cone 04 Medium Speed Firing Schedule for Kiln..... 14

Table II: Test matrix for study..... 15

Table III. XRF data for unfired and fired uncolored test tiles..... 22

Table IV: XRF data for unfired and fired copper colorant test tiles..... 22

Table V: XRF data for unfired and fired iron colorant test tiles..... 22

# List of Figures

---

Figure 1: Three main components of a crystalline glaze.....	8
Figure 2: Crystals radiating from center nucleus.....	9
Figure 3: Typical firing cycle to produce crystals.....	10
Figure 4: Example of glaze crawling on test tile.....	11
Figure 5: Example of speckling in iron oxide containing glaze test tile. Notice the lack of crystals on the surface.....	11
Figure 6: a. Picture of a more needle-like crystal formed at a higher soaking temperature. b. Picture of more fan shaped crystals formed at a lower soaking temperature. This also shows the halos that form around the crystals.....	12
Figure 7: Differences in crystal characteristics due to clay body effects. Not only are the crystals difference sizes, but the colors have changed as well. There were two different kinds of porcelain used (a, b).....	13
Figure 8: The two different programmed firing schedules used in this experiment.....	15
Figure 9: Each dot represents a crystal nuclei.....	16
Figure 10: Measuring grain size using computer software.....	16
Figure 11: a. Uncolored glaze test tile. b. Copper colored glaze test tile. c. Iron colored glaze test tile.....	17
Figure 12: Number of nuclei formed vs. the firing rate for the uncolored, Fe colored, and Cu colored glazes.....	18
Figure 13: Grain size number for the uncolored, Fe colored, and Cu colored glazes at both fast and slow firing rates.....	19
Figure 14: XRD scan of unfired Cu colored glaze. Red peaks indicate the presence of silica ( $\text{SiO}_2$ ) while green peaks indicate the presence of zinc oxide ( $\text{ZnO}$ ).....	20
Figure 15: XRD scan of fired Cu colored glaze. Red peaks indicate the presence of zinc silicate ( $\text{ZnSiO}_4$ ).....	21
Figure 16: Scan of unglazed tile with scan of unfired glazed tile overlayed. Peaks did not line up indicating that the clay body wasn't being pick up by the scan.....	21
Figure 17: Bar graph of XRF data for all samples (LE not shown in graph).....	23
Figure 18: Edge of crystals produced lighter colors in the uncolored samples.....	23

# Introduction

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Crystalline glazes are a type of ceramic glaze which are commonly used to seal or decorate clay pottery. Due to their composition and a specific firing schedule allows crystals to form within the liquid glaze to decorate the the piece being glazed. Crystalline glazes have been around since the Ming Dynasty (1368-1644) but were difficult to produce and control and have been for hundreds of years. These glazes have become more popular recently due to advances in kiln technology and computerized temperature controllers.<sup>1</sup> Even so, crystalline glazes are still difficult to produce and control because of a specific composition and firing schedule along with numerous other factors that affect their growth. This project aims to quantify how certain factors affect the nucleation and growth of these crystals.

## Broader Impacts

The process of glazing and firing a crystalline glaze piece piece can take upwards of 20 hours. A mistake or change in any one of the factors affecting the glaze can cause drastic changes to the behavior of the glaze and may even ruin the piece. Trial and error is usually used to determine the best glaze composition and process. If it was understood how each factor could be adjusted to specifically affect the growth of the crystals, it would make the process much simpler and with less trial and error. The success rate of the fired pieces would also be much higher if the factors affecting the growth of the glazes were better understood. Other times crystals are not wanted in a glaze so it would be beneficial to know what promotes or hinders their growth.

The broader impact is not just limited to the manufacturing of the ceramic pieces but also economic considerations. Crystalline glazes can be somewhat costly, especially depending on the composition of the glaze (\$71.85 per gallon from Laguna Clay)<sup>2</sup>. Repeated trial glazings not only require a substantial amount of glaze materials, but also a substantial amount of kiln time. Running the kiln for long periods of time consumes large amounts of energy which can cost the potter a fair amount of money. For the department's kiln, the estimated cost of a firing would be approximately \$3.59. A larger kiln, used by professionals would run about \$17.97 per firing. This does not include the costs of replacing kiln elements or shelves due to wear which can further increase the costs.

Research has been conducted on the effects of temperatures and firing rates but not much research has been focused on the growth rates of glazes with different colorant concentrations and glaze thicknesses.<sup>3</sup> This project would further add to the current literature regarding crystalline glazes and provide a different view on the effects of colorants on these glazes.



# Background

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## Crystalline Glazes

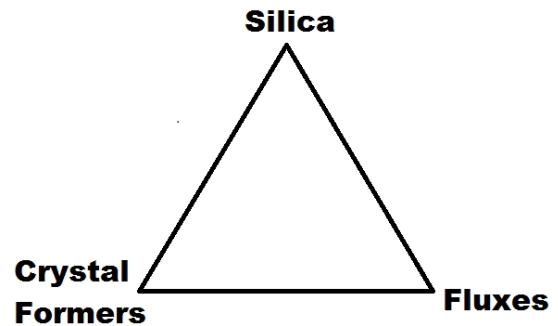
### Basic Composition

A basic crystalline glaze is made up of three main components: silica, fluxes, and crystal formers (such as zinc oxide) (Figure 1). Silica is the base material for ceramic glazes and can form glass all by itself.<sup>4</sup>

However, it melts at temperatures too high for ceramic kilns and must be combined with other materials to reduce the melting temperature.

Approximately one half of the glaze is composed of the silica and the crystal former. These two ingredients, silica and zinc oxide, form zinc silicate (which is the type of crystal looked at in this study).<sup>1</sup>

No matter what crystal forming mineral is used, it needs to be present in the glaze beyond the supersaturation point to form crystals. The remaining balance of the glaze are the fluxes which lower the melting temperature of the glaze. This helps to decrease the viscosity of the liquid glaze during firing and allows for more diffusion to occur, which is critical for the formation of crystals. Some common fluxes are sodium and potassium based fluxes along with metal oxides such as zinc or iron.



*Figure 1: Three main components of a crystalline glaze.*

Crystals can only form if these ingredients are in the right proportions. It differs from other ceramic glazes in part due to the lack of alumina ( $\text{Al}_2\text{O}_3$ ), magnesium oxide ( $\text{MgO}$ ), and calcium oxide ( $\text{CaO}$ ), which increase the viscosity of the glaze (which is why they are commonly used as glaze stiffeners). They are added to glazes to prevent the glaze from running during firing, however, they inhibit the growth of the desired crystals and are omitted from crystalline glazes since the glaze must be fluid enough to form crystals. Decreased fluidity allows less diffusion to occur which causes little or no crystal formation.

### Other Additives

Different compounds can be added to the glaze to achieve different effects or change the properties of the glaze. Since silica is transparent when melted, metallic oxides can be added to color or to change the behavior of the glaze. The crystals collect any pigment or coloring ions in the glaze. Some common oxides are chromium, cobalt, copper, iron, manganese, nickel, and rutile (titanium). The amount of oxides in the glaze usually ranges between 0.5% and 5%. These oxides can affect the melting point of the glaze (which is why they may also be used as fluxing agents.). They can also affect the nucleation or growth of the crystals in the glaze. Colorants can be combined to produce unique color and crystal combinations.

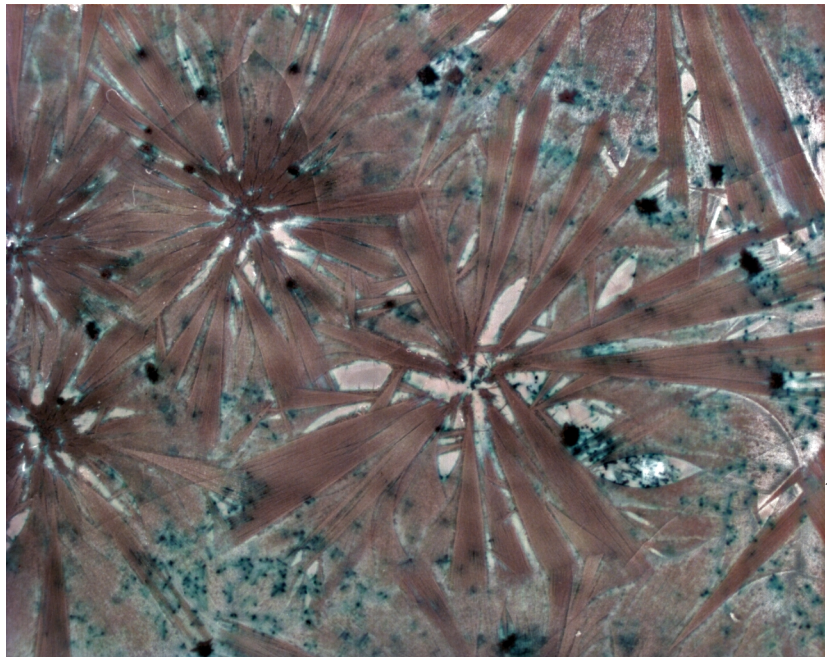
The properties of the raw glaze can also be changed with different additives. Control is needed over the thickness and evenness of the applied glaze to have any degree of reproducibility.<sup>5</sup> Rheology modifiers are used to control settling of the glaze, wetting properties, bonding to the clay body, drying time, and many other properties of the raw glaze. Deflocculants are added to the glaze to help suspend solid particles and help control the dispersion of these particles. Deflocculants work by

attracting, through their charge, water and clay molecules to form a spherical and larger particle known as a clay micelle. The lower density and more bulky shape makes it much more difficult to move freely in the liquid, thus allowing a better dispersion of particles in the glaze and requiring less liquid to suspend the same amount of particles. A commonly used deflocculant is sodium nitrite. Suspension agents are also added to the glaze to suspend the heavier particles in the glaze. Clays, such as kaolins and montmorillonites, are the most common suspension agents. Up to 12 wt% of kaolins can be used as suspension agents, but montmorillonite clays require much less (0.5-2 wt%).<sup>5</sup> Finally, different effects such as matting, opaque, or opalescence can be obtained through the addition of different compounds.

## Crystal Formation

There are two main types of crystals found in glazes: microcrystalline and macrocrystalline. Microcrystalline glazes contain crystals that are invisible to the naked eye and are found in matte and opaque glazes. Macrocrystalline glazes contain crystals large enough to see with the naked eye. Crystal formations occurs in two steps: the atoms arrange themselves to form a nucleus then additional groups of atoms attach themselves to the nucleus to grow the crystal.<sup>6</sup> The seed crystal is commonly a zinc silicate crystal or zinc titanate crystal, if titanium is present in the glaze. A single “crystal” is actually made up of thousands of needle-like crystals which grow out from the center nucleus (Figure 2). Repeated small angle branching of these crystals causes the crystals to fan out and produce “flower-like” shapes.

The growth of crystals takes places in the cooling-soaking cycle of the firing. This soaking period has to provide enough time for the crystal-forming bonds to be attracted to one another and arrange themselves in the crystals. Along with a long soaking time, the temperatures must be high enough to allow the glaze sufficient mobility, which is why crystalline glazes are commonly high-fire glazes. Finally, in order produce crystals, the composition of the crystal must be different from the glaze and the crystal-forming material must be in excess of the saturation limit.



*Figure 2: Crystals radiating from center nucleus.*

## Firing Schedule

A special cooling cycle is a key part of forming crystalline glazes.<sup>1</sup> The firing schedule is made up of three main parts: the ramp up, cool down, and soak (hold) (Figure 3).

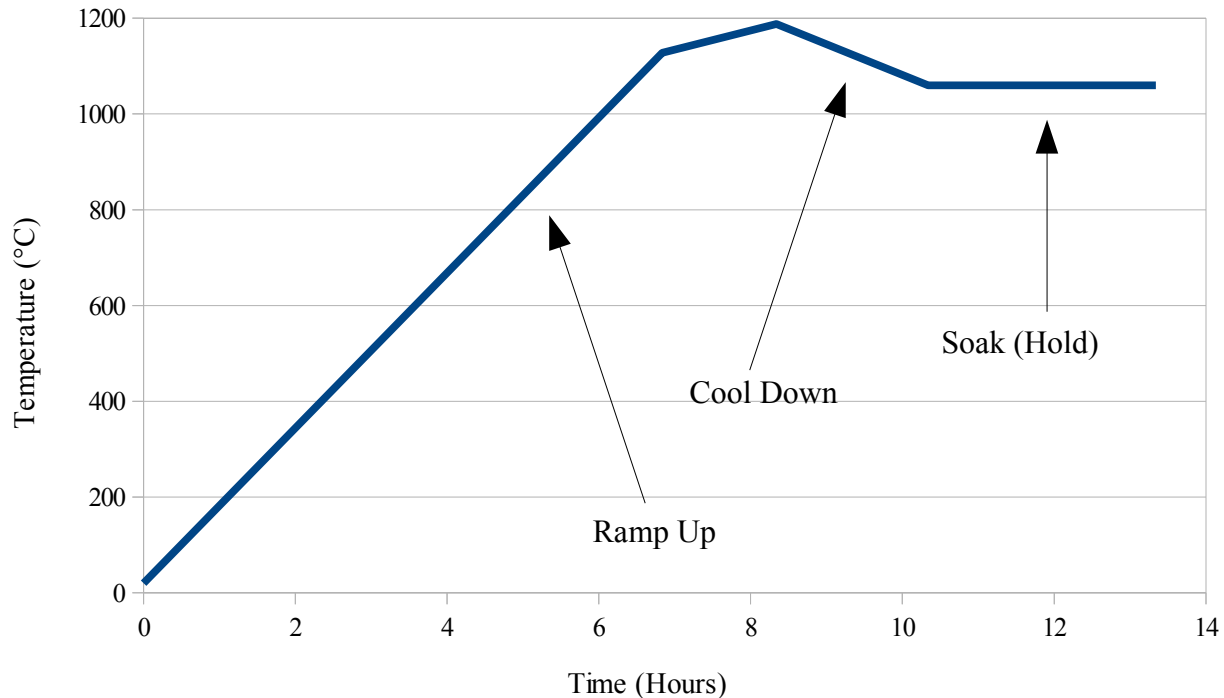


Figure 3: Typical firing cycle to produce crystals.

During the ramp up, the glaze is brought up to a peak temperature which melts the glaze and causes the crystals to dissolve. The crystals form during the cool down/soak period and this must provide enough time for the crystals to form and grow. During the cool down period, crystals start to precipitate out of the glaze solution and the amount of nuclei are affected by the rate at which the temperature is dropped and the difference between the peak and holding temperature. During this period, the glaze is extremely fluid and allows for diffusion of the molecules to produce crystals. There is a temperature range for the nucleation and growth of these crystals. If the glaze is fired at temperatures above the range, the crystals dissolve into the glaze. However, if the glaze is fired at temperatures below the range, there is not enough mobility in the glaze to cause the growth of crystals. Between this range, crystals grow but at have different characteristics depending on the holding temperature.

## Common Problems

Other than the obvious problem of crystals not forming, there are multitude of other problems that plague crystalline glazes along with all other types of glaze. Incorrect glaze-clay body fit can cause defects, such as crazing or shivering and are caused by differences in the coefficients of thermal expansion of the clay and glaze. Crazing is when cracks develop in the fired glaze because the glaze is too small for the clay body (coefficient of expansion of glaze is greater than that of clay body). Crazing can occur when the glazed object is removed from the kiln or it may develop over time. If a

glaze has crazing on the surface, it is not safe for use with food because bacteria can collect and grow in these areas. One way to combat crazing would be to fire at a higher temperature or having a longer soaking period at the end of the firing cycle.<sup>7</sup> Crazing can also be reduced by trying to modify the coefficient of expansion of either the clay or glaze. The addition of silica, boron, or alumina to the glaze can reduce the coefficient of expansion to better match the clay body. The addition of silica in the clay body can also help to reduce crazing.

Shivering is when the glaze flakes off the surface because the glaze is too large for the clay body (coefficient of expansion of glaze is less than that of clay body). This effect is commonly seen around the rims and edges of fired objects. Similar to crazing, shivering is not safe to use with food due to bacterial growth and flakes of glaze breaking off the surface. To combat the effect of shivering, the silica content can be reduced in the glaze or clay body.<sup>8</sup>

Poorly applying the glaze to the clay body can cause defects such as blistering and crawling. Blistering is when vaporization of the gases from the clay and glaze causes bubbles in the glaze and can form marks resembling “craters” on the finished glaze. The most common cause for this effect is applying an extremely thick layer of glaze. To help combat this effect, the greenware can be bisque fired to remove some of the trapped gasses or to apply a thinner coat of glaze. Crawling is when the glaze separates from itself, leaving bare spots on the surface of the clay (Figure 4). It can also be caused when too thick of a glaze coat is applied, but may also be caused by applying glaze to clay that is “dirty.” To help prevent crawling, the ceramic piece needs to be clean before glazing and the glaze needs to be applied in thinner coats.



Figure 4: Example of glaze crawling on a test tile.

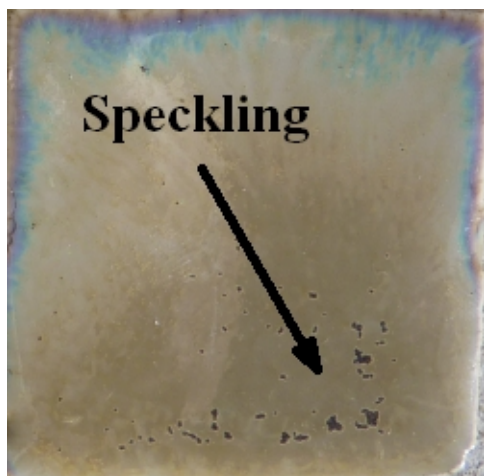


Figure 5: Example of speckling in iron oxide containing glaze test tile. Notice the lack of crystals on the surface.

Speckling is caused by an incomplete mixing of the glaze which can cause “specks” to form in the glaze. Although sometimes this effect is desired, a poorly mixed glaze usually leads to little to no crystal formation (Figure 5).

## Factors Affecting Growth of Crystals

A multitude of factors affects the growth of crystals in glazes including, but not limited to: clay composition, glaze composition, type of nucleus in crystal development, glaze thickness, colorants in the glaze, firing time, maturation temperature, soaking time at maturation temperature, character of kiln atmosphere, impurities in the kiln' atmosphere, and cooling cycle. However, the two most important factors in crystal growth are glaze composition and firing schedule.<sup>1</sup>



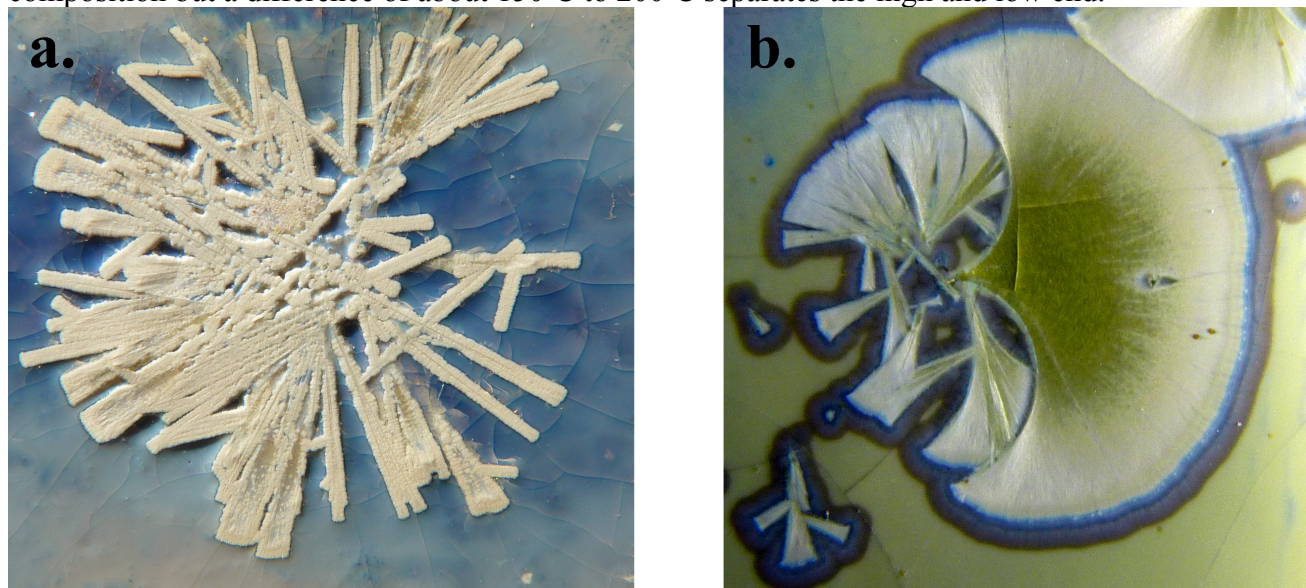
## Glaze Composition

Glaze composition has the largest effect on the nucleation and growth of crystals in a glaze. If the right combination of materials are not present in the glaze, crystals will not form. The composition of the glaze can influence the number, size, color, pattern and shape of the crystals in the fired glaze. Colorants, which are commonly metallic oxides, are typically added to crystal glazes and are easier to adjust than other ingredients.<sup>6</sup> Since zinc silicate crystals are white, colorants are added to either color the crystal or background of the glaze. Due to the molecular structure of the crystals, only certain colorants (cobalt, nickel, copper, iron, and magnesium) are able to move into the crystal structure alone.<sup>6</sup> For example, cobalt takes precedence over other colorants such as magnesium and copper and will move into the crystal structure alone. However, copper will color both the crystal and glaze matrix evenly. Aside from their influence on the color of the glaze, they can also have an effect on the crystals themselves. Iron, for example, will promote larger crystal growth (if under 2%) while titanium creates smaller, but more evenly distributed crystals in the glaze.<sup>6</sup>

To ensure crystals will form in the glaze (assuming the correct glaze and conditions), seeding agents can be added to the glaze. These are commonly added to glazes where it is difficult for nuclei to form. Some common seeding agents are titanium, zinc oxide, zinc silicate, and vanadium. Titanium, for example, is a strong nucleating agent in zinc based crystalline glazes. The seeding material does not have to be the same composition as the crystals forming in the glaze, they just provide a site for the crystals to nucleate. This causes heterogeneous nucleation, or nucleation on imperfections in the glaze or on the clay body. There are multiple ways to apply the seeding agents to the glaze such as adding it to the liquid glaze or can be “glued” to the surface of the applied glaze. Seeding produces much more controlled and consistent results than non-seeding.

## Firing Schedule

The firing schedule has a large effect on the characteristics of the crystals that form. At the top of the crystal growing temperature range, needle-like crystals form (Figure 6a). The low end produces more fan/flower shaped crystals (Figure 6b). The exact temperatures depend on the glaze composition but a difference of about 150°C to 200°C separates the high and low end.



*Figure 6: a. Needle-like crystal formed at a higher soaking temperature (uncolored on red tile). b. fan shaped crystals formed at a lower soaking temperature. This also shows the halos that form around the crystals (Cu colored)*

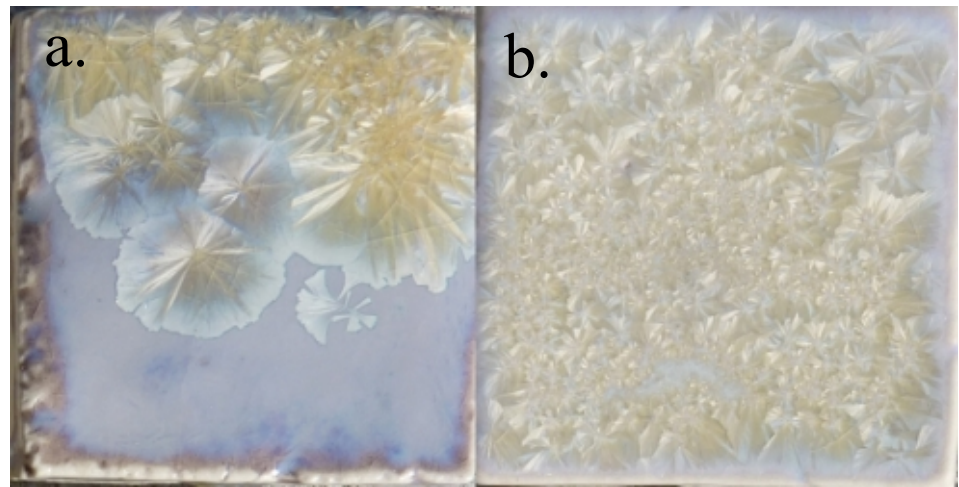
Varying the temperature during holding produces halos, or bands of different colors, on the edge of the crystal (Figure 6b). The faster the drop in temperature between the peak and soaking temperature, the more nuclei that will form on the surface. Fast firing produces more crystals because it cuts down the absorption of alumina and other materials from the clay body. Alumina prevents crystallization because it increases the viscosity of the melted glaze and which inhibits crystal growth.

The colorants can also be affected by the firing schedule. Colorants can produce different colors at different temperatures and in different kiln atmospheres. Iron oxide can produce yellows in oxidizing atmospheres for most temperatures but purple in high temperature reduction firings. Also, some colorants are volatile and will dissipate into the kiln atmosphere if temperatures are too high.<sup>9</sup>

## Other Factors

While the glaze composition and firing schedule are the most important factors to consider when producing crystals, factors such as clay composition, glaze thickness, and the kiln atmosphere can also have a significant effect. Clay composition can change the behavior and look of the crystalline glaze (Figure 7). In this case, the change in clay body from 7b to 7a caused a yellowing of the

crystals, an increase in crystal size, and less uniform coverage. At high firing temperatures, clay body materials can diffuse into the glaze. Such compounds as alumina ions, salts, and metallic oxides can be absorbed into the glaze which can change the character or formation of the crystals. Some clay bodies may not be able to produce crystals due to the leaching of certain crystal inhibiting



*Figure 7: Differences in crystal characteristics due to clay body effects. Not only are the crystals difference sizes, but the colors have changed as well. There were two different kinds of porcelain used.*

compounds into the glaze. Most white/lighter clay bodies will not interfere with crystal growth.<sup>6</sup>

Glaze thickness also has an effect on the crystal growth in the glaze. Crystalline glaze application requires thicker coats than usual on clay pieces due to its fluidity during firing. However, the glaze application cannot be too thick as to cause problems such as crawling or blistering. It is recommended that the glaze be applied to the thickness of a dime.<sup>6</sup> Spraying is the recommended method of applying the glaze; however, brushing and dipping are also used. When brushing on the glaze, multiple thin coats are used. Regardless of the application method, the glaze should be thicker at the top of vertical surfaces due to the fluidity of the glaze during firing.

The kiln atmosphere can also affect the crystal growth in a glaze. Crystalline glazes are typically fired in an oxidizing atmosphere. Reduction atmospheres produce more tension within the glaze which may inhibit the growth of crystals.<sup>6</sup> The reducing atmosphere can also cause the reduction of zinc oxide at temperatures above 950°F which allows the zinc metal to boil off. However, reduction

atmospheres can be used at the end of the firing cycle after crystals have formed and at lower temperatures to produce different colors or surface effects.

## Experimental Procedures

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### Sample Preparation

#### Clay Tiles

Tiles were formed using an arbor press and an aluminum mold with dimensions of 2" x 2" x 3/8". A white porcelain clay, Hagi Porcelain (WC-861) from Laguna Clay Company, was used to make the tiles. The clay was placed into the mold and the arbor press was used to compact the clay into the mold. Plastic wrap was used to prevent the clay from sticking to the mold and to make it easier to remove the tile from the mold. The excess clay was removed by hand from the edges and the tiles came out smooth and uniform. As formed, the tiles were 2" x 2" x 3/8". The wet clay tiles were placed between two sheets of drywall to prevent warping while drying with a secondary effect of helping to pull moisture out of the tiles. After drying for approximately one week between the drywall sheets, the tiles were fired in the kiln to cone 04 using the preprogrammed setting in the kiln. (Table I).

*Table I: Preprogrammed Cone 04 Medium Speed Firing Schedule for Kiln<sup>10</sup>*

Segment	Rate (°F/hr)	Temperature (°F)	Hold
1	93	121	0
2	204	538	0
3	82	621	0
4	149	923	0
5	49	1063	0

This bisque firing helps to remove most of the chemical and mechanical water and to prepare the tiles for glazing. Bisque firing around 1000°C gives a suitable amount of porosity (greater than 30%) which allows for easier glazing allows the glaze to adhere better to the surface.<sup>11</sup>

#### Glazing

The base glaze used is the Lavender Filigree crystalline glaze (WC-160) purchased from Laguna Clay Company. This was used as the uncolored glaze. To produce the colored glazes, 1 wt% (dry glaze) of iron oxide and copper oxide was added to the uncolored glaze and mixed in a food processor for five minutes to promote an even distribution of oxide throughout the glaze. Iron and copper oxide are two of the most popular colorants for ceramic glazes. The glaze was applied to the tiles using a 1" paint brush. One layer was brushed on, allowed to dry for approximately two minutes, followed by another layer of the glaze. This process produced an even and uniform coat across the surface. After glazing, the tiles were immediately placed into the kiln and fired.

## Firing

The kiln used for firing is a Skutt Kilnmaster 614-3 kiln. The tiles were placed on clay catch trays and were fired to cone 5 using a two different firing schedules to promote crystal growth (Figure 8).

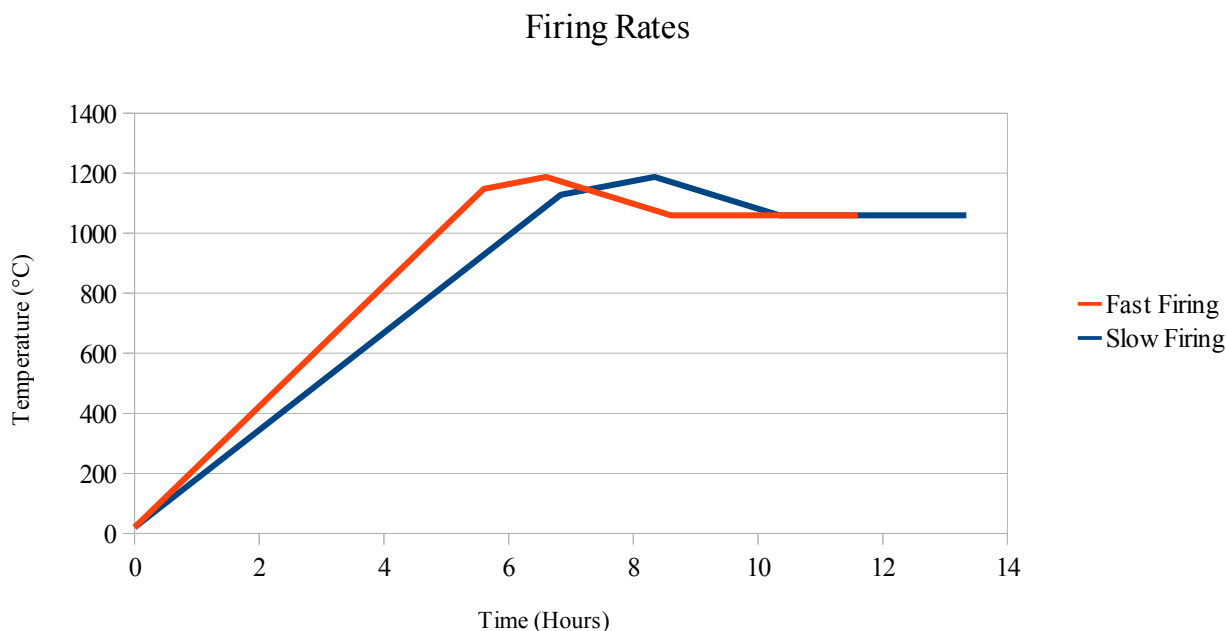


Figure 8: The two different programmed firing schedules used in this experiment.

The only difference between the two firing schedules was the ramp up rate. The slow firing rate took 8.35 hours to reach peak temperature while the fast firing rate took 6.6 hours. This meant that the total firing time was 1.75 hours longer for the slower firing time.

Two levels were used in the kiln so that a total of 12 samples could be fired at one time (4 of each color). The samples were placed into the kiln using a random number generator to negate the effects of hot spots in the kiln. A total of 7 trials were done at each firing speed for a total of 28 samples for each combination of firing speed and colorant (Table II).

Table II: Test matrix for study.

	Fast Firing	Slow Firing	Total
Uncolored	28	28	56
Copper	28	28	56
Iron	28	28	56
Total	84	84	168



## Data Collection

Since there is no standard way to characterize the crystals, different methods were adapted and applied to the crystals in the glaze.

### Number of Crystal Nuclei

The samples were scanned into an image format using a flatbed scanner. A total of 20 of each colorant were counted, with 10 from each firing speed. The cell counting feature in the ImageJ software<sup>11</sup> was used to manually count the total number of nuclei in the samples (Figure 9). The software kept track of the number of nuclei selected. If the nuclei were too numerous to count, the nuclei were counted on three smaller areas on the surface (200 pixels by 200 pixels at 2x) which were randomly selected. This value was then averaged to the entire sample.

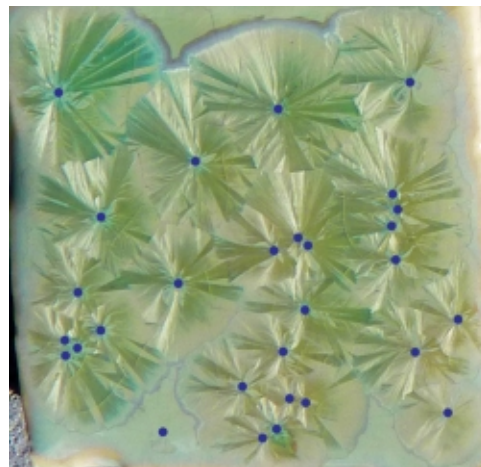


Figure 9: Each dot represents a crystal nuclei.

### Crystal Size

The crystal size was determined by using the intercept method which is described in ASTM E112. This procedure is

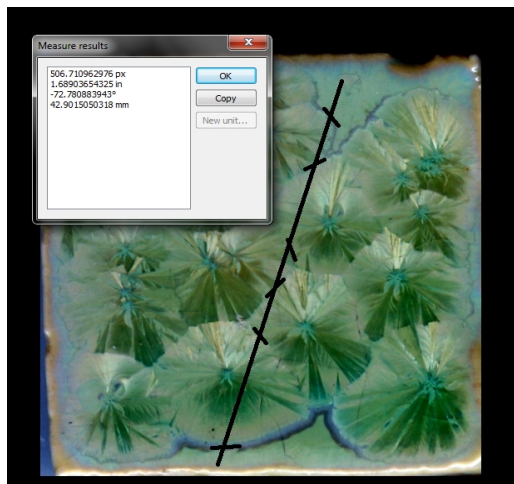


Figure 10: Measuring grain size using computer software.

used to calculate the ASTM Grain Size Number, but was adapted to characterize the size of the crystals in this experiment. Using imaging software, straight lines were drawn across the samples in random orientations. The number of intersections between the line and the edges of the crystals was counted (Figure 10). Lines were drawn until the total number of intersections,  $P$ , was greater than 30. The total number of intercepts was then divided by the total length of the lines drawn,  $L$  to get a value  $P_L$ . Using formula (1), the ASTM Grain Size Number,  $n$  was calculated.

$$n = -3.3 + \log_{10}(P_L) \quad (1)$$

The more intercepts per length would produce larger  $P_L$  values and thus a larger  $n$  value. It should be noted that the

larger the  $n$  value, the smaller the crystals.

### X-Ray Diffraction (XRD)

Using the Siemens D5000 XRD machine with  $\text{CuK}\alpha$ , XRD analysis was conducted on one sample of each type of glazed tile, both fired and unfired. An unglazed tile was also tested. The test tiles were loaded into the machine as flat as possible. The samples were scanned from  $10^\circ - 120^\circ$ , with an increment of  $0.05^\circ$  and a scan speed of 2 deg/min. The power for the scans was 40 kV and 40 mA with a scan type of "locked couple scan". Using the provided software, peaks were matched with substances in the database. Since the x-rays only penetrate 100-150  $\mu\text{m}$ , the scan should only pick up the glaze and not the clay body. This testing looked for the presence of zinc oxide and silica in the unfired glaze, zinc silicate in the fired glaze, and the presence of the colorant oxides in both the fired

and unfired.

### X-Ray Florescence (XRF)

Using the Innov-X Systems XRF unit, XRF data was taken on unfired and fast firing samples to determine elemental quantities in the glaze. The XRF uses x-rays to excite electrons in the material which causes them to fluoresce and release x-rays. The detector picks up these electrons and determines elemental composition. The instrument was calibrated using a piece of 316 stainless steel. Two readings were taken on each type of glazed tile, both fired and unfired which were then averaged. The samples were scanned using the “analytic mode.” The software then calculated the percent elemental composition for the glaze. The detector can not pick up elements lighter than Ti, so this was used to look for both the colorants along with zinc. The scan depth of 3-10  $\mu\text{m}$  will not pick up the underlying clay body.

## Results

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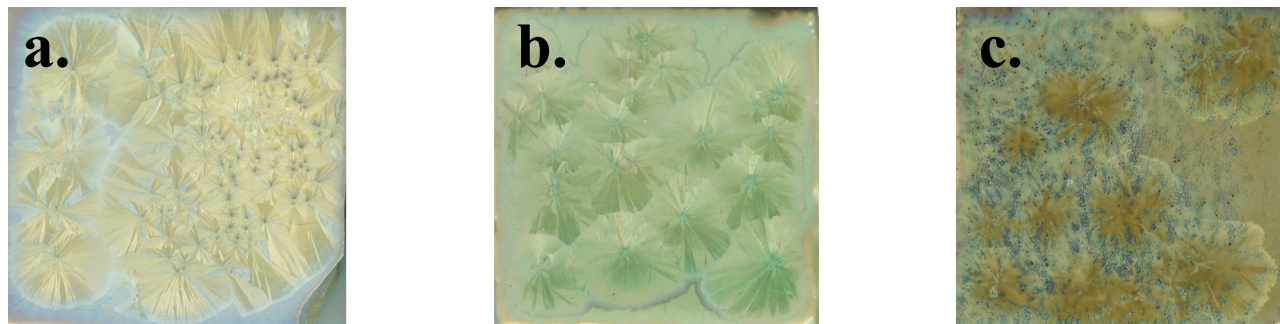
### Crystal Shape and Color

The uncolored glaze produced small faint-yellow tinted crystals on a faint-blue background. The crystals were flower shaped, however, there were so many crystals that their growth was impeded (Figure 11a).

The copper colored glaze produced green crystals on a green background. On the edges of the crystals, a bluish halo formed. These crystals were also flower shaped (Figure 11b).

The iron colored crystals produced brown crystals surrounded by larger pale brown halo regions intermixed with blue areas. The background was a light brown color. (Figure 11c).

Crystals did not nucleate near the edges of the tiles in nearly all of the samples but the crystals did grow towards the edges.



*Figure 11: a. Uncolored glaze test tile. b. Copper colored glaze test tile. c. Iron colored glaze test tile. All were fired at the same time under fast firing conditions.*

## Crystal Nuclei

Both the firing rate and colorant oxides had an effect on the amount of crystal nuclei formed on the surface of the tile (approximately 3.24 in<sup>2</sup>) (Figure 12).

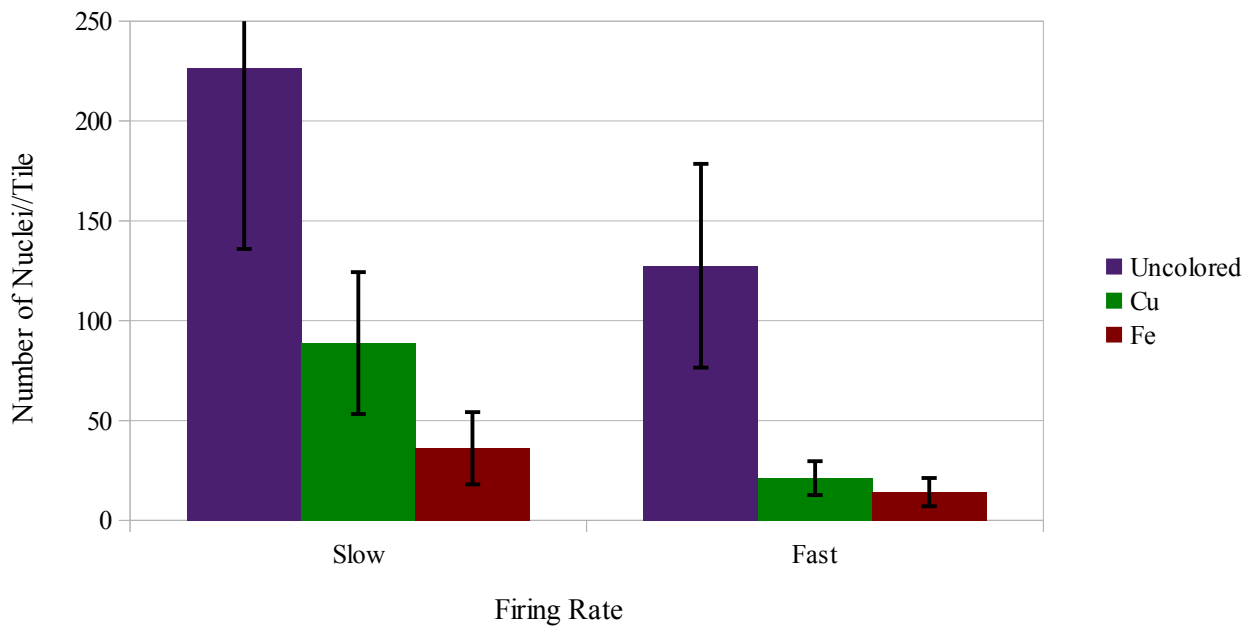


Figure 12: Number of nuclei formed vs. the firing rate for the uncolored, Fe colored, and Cu colored glazes.

The slower firing rates produced more nuclei for all compositions and the addition of colorant oxides reduced the amount of crystals in both firing rates. The uncolored glaze produced the most nuclei in both cases and iron producing the least amount of nuclei. The addition of copper and iron oxide to the uncolored glaze under fast firing conditions decreased, on average, the number of nuclei by 60.1% and 84.0% respectively. Under slow firing conditions the number of nuclei dropped by 83.4% for the copper and 88.9% for the iron on average. The change from the slow to the fast firing rate caused a 43.8% reduction in the uncolored samples, a 76.13% reduction in the copper colored samples and a 61.0% reduction in the iron colored samples on average.

## Crystal Size

The slower firing rates produced smaller crystals (larger grain size number means smaller crystals) for all compositions and the addition of colorant oxides increased the size of the crystals in both firing rates (Figure 13).

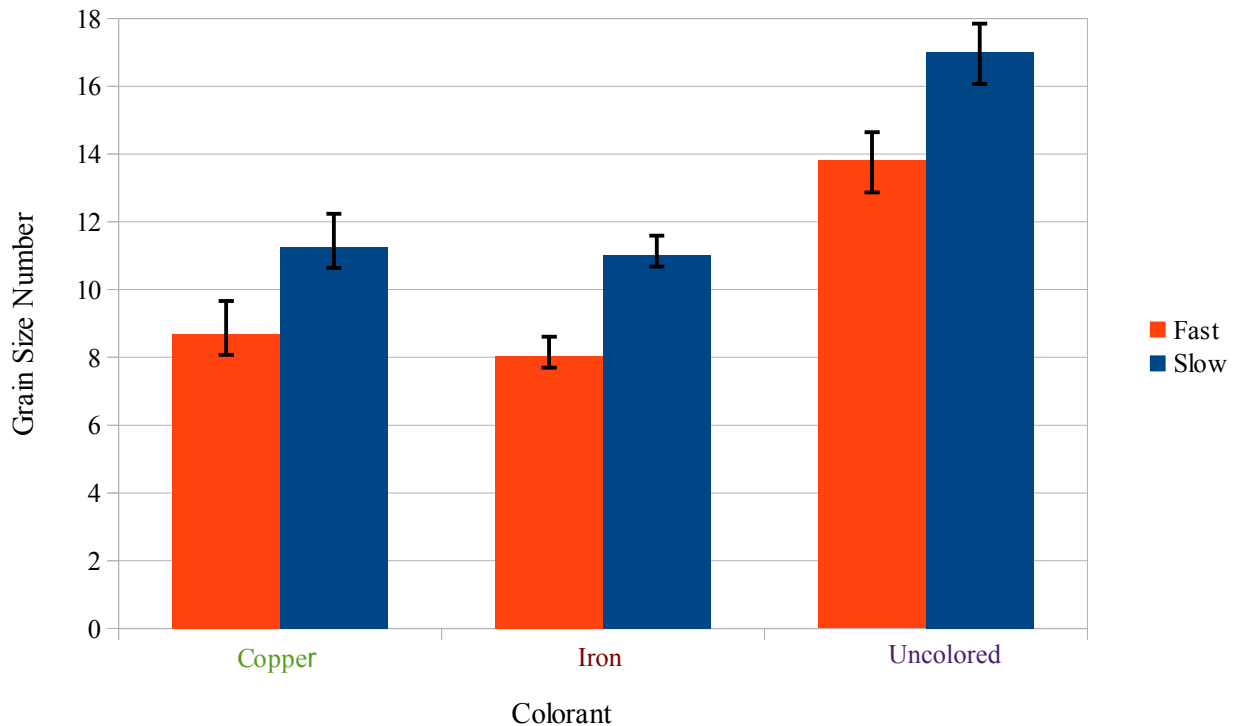


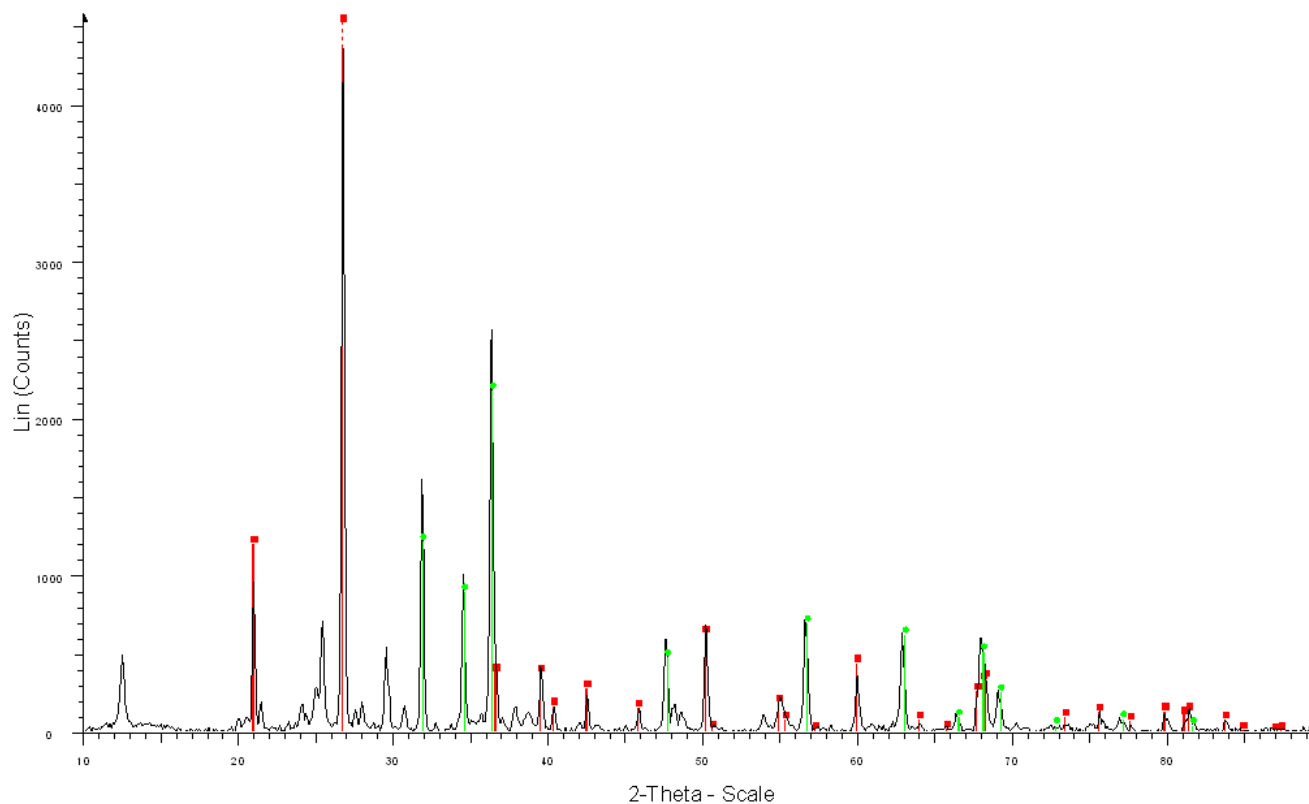
Figure 13: Grain size number for the uncolored, Fe colored, and Cu colored glazes at both fast and slow firing rates.

The uncolored glaze produced the smallest crystals in both cases with copper colorant producing a decrease of 37.1% in the grain size number with iron colorant producing a 41.8% decrease in the grain size number (increase in crystal size) for the fast firing rate on average. The slow firing rate produced a 33.8% reduction in the grain size number for the copper colorant and a 35.2% reduction in the grain size number for the iron colorant on average. The change from slow to fast firing rate decreased the grain size number in the copper colored by 22.8%, iron colored by 27.0% and uncolored by 18.8% on average.

## X-Ray Diffraction (XRD)

### Unfired Tiles

XRD scans of the unfired test tiles showed the presence of both silica (quartz) ( $\text{SiO}_2$ ) and zinc oxide (zincite) ( $\text{ZnO}$ ) through the matching of peaks (Figure 14).



## Fired Tiles

XRD scans of the fired test tiles showed the presence of zinc silicate ( $\text{ZnSiO}_4$ ) in the glaze through matching of peaks in the database (Figure 15).

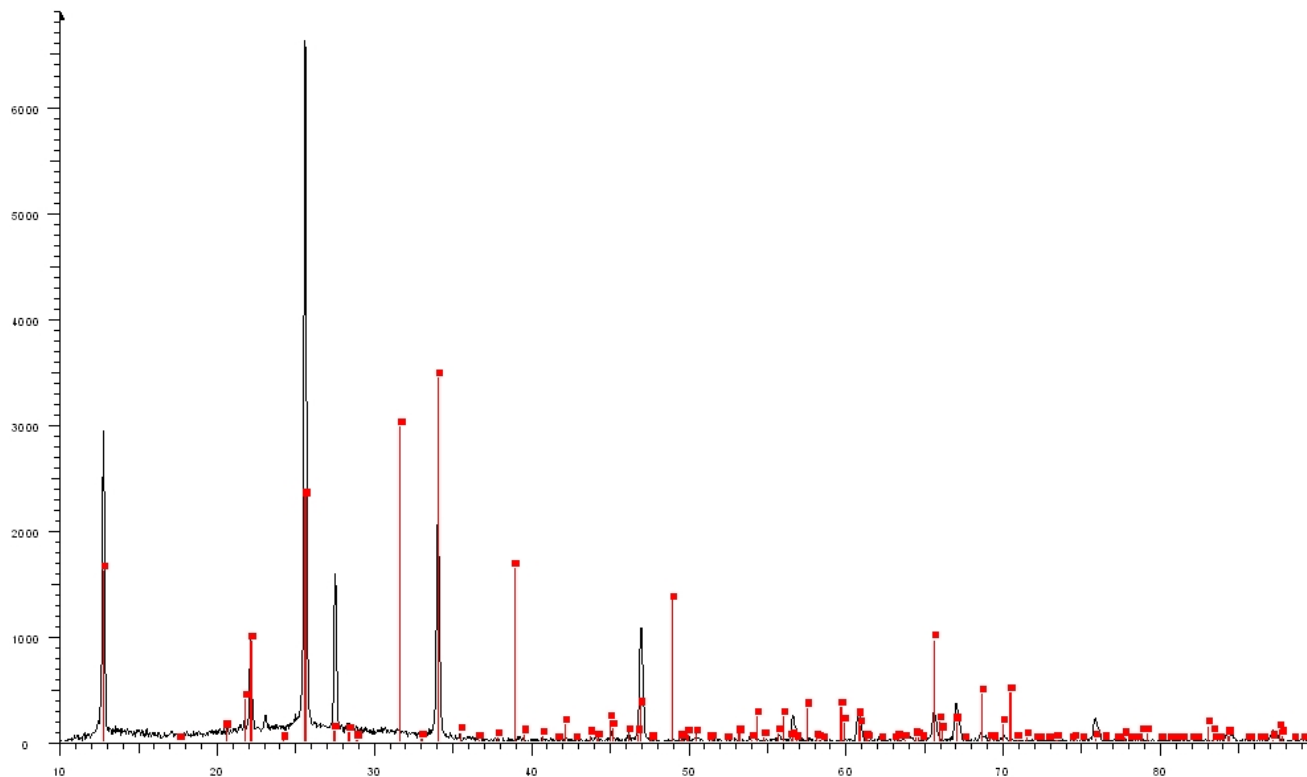


Figure 15: XRD scan of fired Cu colored glaze. Red peaks indicate the presence of zinc silicate ( $\text{ZnSiO}_4$ ).

Not all of the database peaks matched up with the scan. However, enough peaks lined up such that the material could be determined to be zinc silicate. This scan also produced much less peaks than the previous scan of the unfired tiles. All three of the colors produced similar scans.

## Additional XRD Results

Diffraction scans were also performed on both copper and iron oxide powder. These scans were overlayed on the glazed tile scans but no peaks were matched between the two diffraction patterns. This indicated that the oxide concentrations were too small to be picked up by the XRD scan on the glazed tiles. A scan was also performed on an unglazed tile. This was also overlayed on the glazed tile scans and it was determined that little, if any, of the clay body was being picked up by the scan (Figure 16).

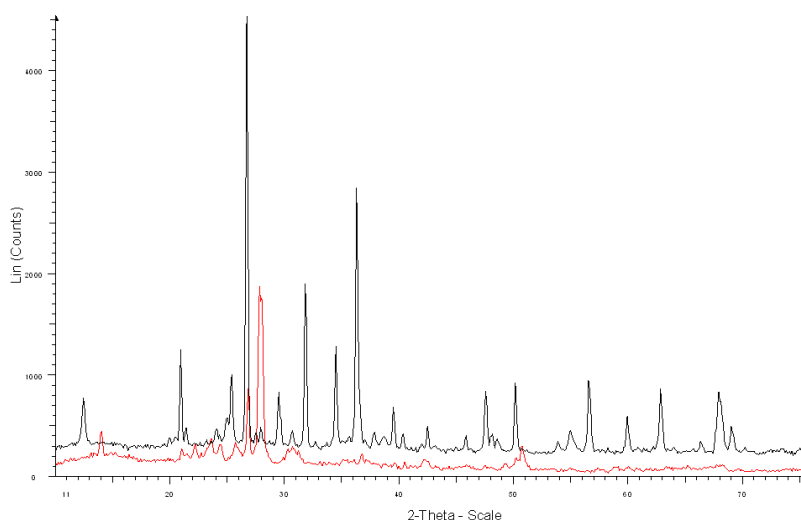


Figure 16: Scan of unglazed tile with scan of unfired glazed tile overlayed.

## X-Ray Florescence (XRF)

### Uncolored

XRF scan of the uncolored glaze showed the presence of some iron, but no copper in the glaze (Table III). The elemental quantities of the lighter elements, iron, and tin increased while the elemental quantities of zinc and titanium decreased after firing.

Table III. XRF data for unfired and fired uncolored test tiles.

	Unfired	Fired
Element	at%	at%
LE	84.39	85.83
Zn	11.84	10.48
Ti	3.58	3.32
Fe	0.14	0.16
Sn	0.05	0.06
W		0.14

### Copper Oxide

XRF scan of the copper oxide colorant glaze showed a presence of copper in the tiles (Table IV). The elemental quantities for lighter elements (LE) and iron increased while the quantities of zinc, titanium, copper, and tin decreased after firing.

Table IV: XRF data for unfired and fired copper colorant test tiles.

	Unfired	Fired
Element	at%	at%
LE	84.64	86.2
Zn	11.14	9.64
Ti	3.39	3.22
Cu	0.59	0.26
Fe	0.09	0.17
Sn	0.06	0

### Iron Oxide

XRF scan of the iron oxide colorant glaze showed a presence of copper in the tiles (Table V). The elemental quantity for zinc increased while the quantities of the lighter elements, titanium, and iron decreased after firing.

Table V: XRF data for unfired and fired iron colorant test tiles.

	Unfired	Fired
Element	at%	at%
LE	86.42	85.46
Zn	9.39	10.63
Ti	3.26	3.04
Fe	0.92	0.86



Among all the samples studied, the elemental quantities for zinc ranged between 9% and 12% while the titanium ranged from 3.0% to 3.60% (Figure 17).

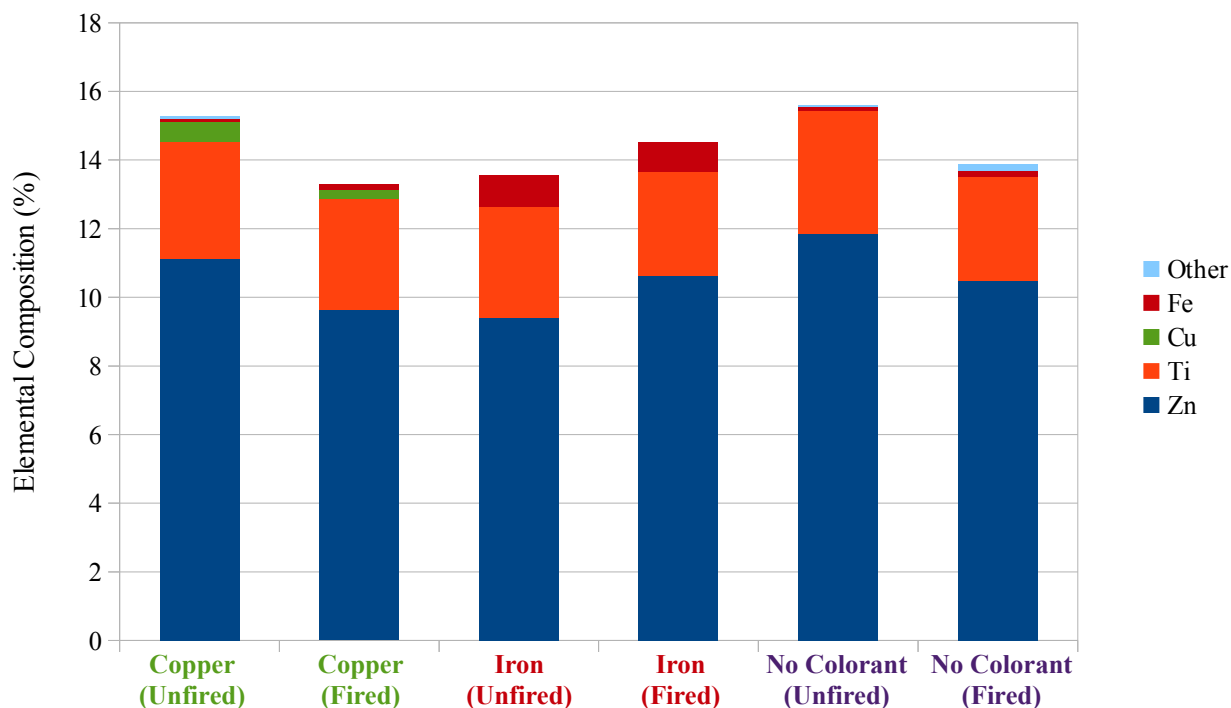


Figure 17: Bar graph of XRF data for all samples (LE not shown in graph).

## Discussion

### Crystal Shape and Color

All crystals formed on the tiles were either flower or fan-shaped crystals which was due to using a soaking temperature on the lower end (1060°C). Typically, changing the soaking temperature can change the overall shape of the crystals which was not done in this experiment. Flower-like shapes were chosen to make it easier to measure and distinguish the crystals. Many crystals also showed

The base glaze produced faint yellow crystals in a white background (Figure 11a). Uncolored zinc silicate crystals are white, so the color in these crystals was from the absorption of oxides from the clay body during firing. An even faster firing cycle produced crystals which were more white. The outer edges of the crystals were typically lighter than the interiors of the crystals (Figure 18). The colorants were

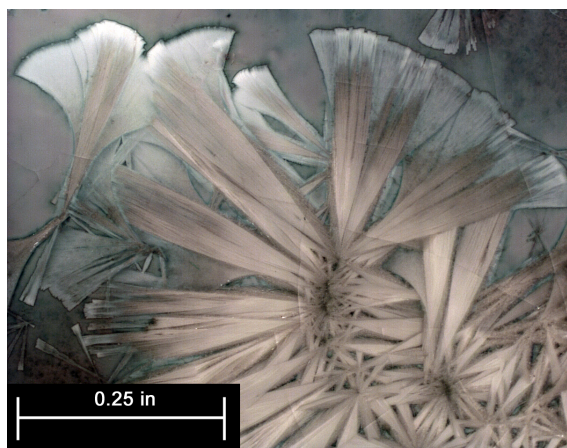


Figure 18: Edge of crystals produced lighter colors in the uncolored samples.



incorporated into both the crystal and the glaze matrix, however, they each had different effects.

The copper oxide colored both the inside of the crystal and the glaze with a similar color (interior of crystal was darker and tended to have a more yellow hue). The copper oxide also produced bluish halos where the crystals bordered the glaze matrix (Figure 11b). These halos were not consistent, however, and varied in thickness and color. These halos were formed after the soaking period had ended and kiln was brought down to room temperature. The lower holding temperature causes the oxide to produce a different hue at the edges of the crystals.

The iron oxide also colored both inside the crystal and glaze matrix, but had different characteristics. The glaze matrix was a tan color with blue near the edges of the tiles (Figure 11c). The crystals were multicolored with multiple brown “fans” radiating from the center nucleus with a cream/light brown making up the rest of the flower-shaped crystal. Small blue specks were also contained in the crystal. It is unknown what caused these tiny blue specks.

## Number of Nuclei

The addition of colorants and increasing the ramp up rate reduced the number of crystals formed in the glaze. The colorants within the glaze acted as fluxes to help reduce the melting temperature of the glaze. When the glaze is fired, it is raised to a peak temperature to dissolve most of the zinc silicate crystals. However, the reduced melting temperature allows for even more of the zinc silicate crystals to dissolve in the glaze which provides less places for the nucleation of these crystals.

The increased ramp up rate meant that less overall time was spent at elevated temperatures ( $> 900^{\circ}\text{C}$ ) (Figure 8). This meant that there was less time for diffusion to occur at these temperatures. Less clay body material is able to diffuse into the glaze matrix. Some compounds in the clay body can lead to more nuclei by providing sites for these nuclei to form. Other compounds, such as alumina, can thicken the glaze when fluid. During the soaking period, the decreased diffusion makes it more difficult for nuclei to combine.

The addition of copper and iron oxide to the glaze had a larger effect on the amount of nuclei formed than the ramp up rate. The fluxing affect caused by the oxides outweighed the effects of alumina being absorbed into the clay body. A further reduced ramp up rate would be required to negate the effects of the colorant oxides. Also, near the edges of most tiles nuclei did not form. This was due to the glaze running off the sides of the tiles reducing the thickness of the glaze.

## Crystal Size

The addition of colorants and increasing the ramp up rate increased the size of the crystals formed in the glaze. The metal oxides act as fluxing agents within the glaze. These help to lower the melting point of the glaze and also make the liquid glaze less viscous. The decreased viscosity of the melt allows for more diffusion to occur within the glaze. At the same soaking temperature, the greater diffusion in the colored tiles allows molecules to move greater distances within the glaze and form larger crystals. This also gives less total time for the zinc silicate crystals to form from zinc oxide and silica and also for them to dissolve in the liquid glaze. As the zinc silicate crystals grow, the larger crystals grow at the expense of smaller crystals.

The increased ramp up rate meant that less overall time was spent at elevated temperatures ( $> 900^{\circ}\text{C}$ ).

This meant that there was less time for diffusion to occur at these temperatures. Clay body materials such as alumina can cause the glaze to become more viscous and increase the surface tension of the glaze. Alumina is commonly added to ceramic glazes to prevent the glaze from running off the glazed piece, but the increased fluidity is required for the crystals to form which is why it is not added to these glazes. However, alumina can be absorbed into the glaze at elevated temperatures. When the glaze becomes fluid, the glaze attacks the clay body which forms intermediate compounds.<sup>12</sup> These compounds then diffuse into the liquid glaze matrix. The increased viscosity caused by alumina and other compounds reduces the diffusion in the glaze matrix. Less diffusion meant that the crystals could not grow as large because the molecules can not move as great of distances.

The addition of the colorant oxides also had a much larger effect on crystal size than the firing schedule. However, the crystals did impede on the growth of other crystals in the glaze matrix. The increased nuclei lead to more interference and thus smaller crystals. It is not known if the uncolored glaze would produce the same size crystals if not for nearby crystals impeding their growth.

## **X-Ray Diffraction**

The XRD scan on the unfired tiles had excellent matches with both the zinc oxide and silica. However, three mid-sized peaks could not be identified at 12.5°, 25.3°, and 29.6°. Database scans of compounds such as titanium oxide, iron oxide, and copper oxide could not be matched to those peaks. Scans were also run on both the iron and copper oxides to see if peaks could be matched to either samples. The peaks from these scans did not match the previous scans of the tiles. It was determined that the concentrations of the colorant oxides were too low to be detected by the XRD.

The XRD scan on the fired tiles produced a match with zinc silicate, which is the composition of the crystals. However, not all peaks of the database matched with the scan. Large peaks on the database scan at 31.6°, 38.9°, and 48.9° did not show up on the scan. This may be explained by the glassy layer which forms on the surface of the tiles. Scans on sample tiles produced poor results with shifted peaks and the absence of peaks in the scan. An attempt was made to remove this layer by abrading the surface. This produced noticeably better results but still did not match all of the main peaks in the database scan of the zinc silicate. An attempt was also made to remove the glaze from the clay body to produce a glaze powder for the XRD, but it was too difficult to separate the thin layer of glaze from the clay body. The missing peaks could also be caused by the preferred orientation of the crystals within the glaze. The powdering of the samples would help to combat this problem.

## **X-Ray Florescence**

The results from the XRF confirmed the presence of zinc, titanium, and both colorant oxides. In most cases, the concentration of iron in the glaze increased after firing. This was due to the absorption of clay body materials into the glaze. It is also suspected that the yellow tint of the crystals was caused in part by the absorption of clay body materials in the glaze. A different type of white porcelain was tested along with a red clay. This colored the background and crystals in different ways. The white porcelain created even more yellowish crystals. The red clay had a drastic effect which caused white crystals to form on a dark blue background (Figure 6a).

# Conclusions

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This study looked at the effects of colorant oxides and firing rate on the growth and nucleation of zinc silicate crystals in crystalline glazes. Both copper oxide and iron oxide glazes were used, along with the uncolored glaze and fired at two different firing rates. These amount of nuclei per tile and crystal sizes were measured and the glazes were further characterized using XRD and XRF.

1. The addition of iron oxide or copper oxide to the glaze produces significantly less nuclei and larger crystals than the uncolored glazes by a fluxing effect. The fluxing effect caused by the colorants lowers the melting point of the glaze and allows more zinc silicate crystals to dissolve into the liquid glaze, which leads to less nuclei. More diffusion is also able to occur in the glaze which allows for larger crystals to form by decreasing the viscosity of the liquid glaze.
2. The increase in the ramp up rate during firing produces significantly less nuclei and larger crystals by allowing less time for clay body materials to diffuse into the glaze. The decreased amount of clay body materials in the glaze leads to less sites for nucleation and makes it easier for nuclei to combine due to increased diffusion. The decreased amount of clay body materials in glaze reduces the viscosity of the glaze and allows for diffusion to occur over longer distances and thus, larger crystals to form.
3. If colorant oxides are added to a glaze, the ramp up rate needs to be decreased to produce the same sized crystals as in the uncolored glaze.
4. A higher oxides concentration and faster ramp up rate would produce even larger crystals. To prevent impinging, the soaking time could be decreased.

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