Neighborhood of a Glaze

Written by **Carol Marians**

Introduction

Like a beautiful shell on the beach, a miracle out of the kiln. Is this glaze reproducible? And what will be the effect of small changes in composition or firing? More, is this glaze unique, or does it have exciting relatives?

Let me tell you of my adventures exploring the near neighbors of one glaze.

'Neighbor glazes' are those that might result from an error in weighing, or in the mixing of the glaze; they may be the result of using a new bag of an 'old material', a bag whose contents labeled as Custer feldspar was mined a decade earlier than the spar in the just-used-up bag was, and differing from that one's exact composition. Or they result from an intentional tweaking of the glaze by a small amount, for example replacing a potash feldspar with a soda feldspar.

Here I'll describe - and give an example - of a method for exploring the neighborhood of a glaze; a method I call 'axis testing'. It is a controlled way of tossing off darts into black holes.

To explore is to examine effects without worrying whether the result forms a worthwhile glaze or not. The objective is to isolate parameters, draw conclusions, and attribute an effect to a cause.

For example, increasing the silica in a glaze, or increasing both silica and alumina, which then decreases the proportion of the basic components of the glaze (the fluxes) the first column oxides in the seger formula. The result may, as is commonly assumed, result in a stiffer, underfired glaze. On the other hand, the increase in silica will make the glaze flow off the pot as it would in an alkaline matt.

It's all to the good and I have discovered what an increase of silica does in this glaze.

Exploration

The path down a canyon is not a straight drop. The path is 'found' via Reconnaissance, a circuitous route that finds its way along ledges.

What is reconnaissance for glaze development?

I want to test a few glazes, all independent of each other.

There are several established methods of discovering how small changes in a glaze composition affects the fired result.

In a line blend the two end member glazes are mixed in different, planned proportions. In a triaxial blend three 'corner' glazes are mixed in different, planned proportions, and in a biaxial blend four 'corner' glazes are mixed - again in planned proportions. A 5x7 biaxial grid results in 35 glazes, all achieved by the mixing of just four independent glazes.

The making of axial grids requires a lot of measuring, mixing, and application of glaze to test tiles, but in fact they test only a small number of independent glazes. Axial grids demand a lot of work and may provide only the discouraging news that the chosen axis represents oxide components to which the glaze isn't particularly sensitive. By this I mean only that small changes in that oxide does not appreciably alter the appearance of the glaze.

The objective of 'axial testing' is to first find the compositional changes which result in large changes in the glaze. If one has happened upon one strikingly interesting glaze, a Priori, it is unlikely that one has any information of the changes which will most strongly alter the glaze in question.

Axial testing and grid testing have differing objectives. Axial testing is for determining the 'lay of the land', grid testing is for finding the precise location that maximizes desired properties in a region already well known.

If, for example, I want to know the effect of increasing the alumina in a glaze, then one test with a sufficient increase of alumina to be visible will tell me that. The measuring and mixing and application of the intermediate glazes involved in a line blends will give me no additional information.

The tests I describe below involve 12 glazes, each independent of each other. Which means I weigh out 12 glazes but am spared all the measuring and mixing and application (and cleanup) of the intermediate glazes involved in line blends, triaxial blends etc. In this testing of the waters, I am looking for a gross qualitative sense of the effects of small changes in one, at most two, of the component oxides in the empirical formula of that glaze. I am asking *what happens if?* - the open-ended question for which there are many tests.

The axis method of glaze exploration

I want to examine the region of *Glaze X* so I pick some variables, some directions I call axis along which I'll migrate the empirical formula of the glaze. I will reject 'common expectation' of likely results, seeking instead, fortuitous breakthroughs.

The modified glaze composition must be close enough to its starting point to keep the fired change small and interpretable. By altering one, at most two, components in the empirical formula, interpreting results is likelier to be possible.

I examine the effect of a change in silica, and only silica. More silica makes alkaline matt glazes flow but stiffens alumina matt. I am asking whether X behaves like an alkaline matt, an alumina matt, or perhaps neither?

I next investigate a change in the amount of alumina. Now I consider minimalistic changes in the bases.

The empirical formula, or seger formula, consists of the number of moles of each oxide, the weight divided by the molecular weight of that oxide. As the empirical formula is representative of the glaze, it is normalized. Following Seger, it is traditional to divide the molecular weight of each oxide by the sum of the molecular weights of the basic, or first column oxides. As a result of the normalization, the sum of the first column oxides will always be one.

If one first column oxide changes, so must at least one other.

What effect will a change in the relative proportion of alkali metals to alkaline earths do?

The alkali metal oxides are:
K_2O, Na_2O, Li_2O

The other oxides are the alkaline earths:
CaO, MgO, BaO, SrO
and the metalic oxide, ZnO.

What effect would a relative increase of one of the bases have on the others? And what will be the effect on the other basses if there is a relative increase of one of them? Furthermore, what will the change of the relative proportion of total bases in the glaze, which is the equivalent to an increase of both alumina and siilica which preserves the alumina-silica ratio?

Here are the axis which I used for the described tests:

1. silica
2. alumina
3. ratio of alkali metals to other bases
4. maintaining a constant silica/aluminum ratio, with silica and alumina increased or decreased together, relative composition of bases unchanged.

I found these an interesting set of axis for a first survey.

One more remark that must be made, as there will be only one test for each direction, it is necessary to choose carefully. It is important that the increment (either increase or decrease) be sufficiently large that the effect can be seen, and not so large that the result is no longer a viable glaze.

Often changes in alumina will require trading out one feldspar for another, with a shift in the balance of alkali metals.

I found half a dozen line blends whose target glaze is in the middle, then, as a first cut tested only the end members.

The first step is an open-ended survey of the landscape which presents us with an infinite number of possible tests. Open exploration provides us guidance to the eventual *how do I get this?* and on to our eventual goal.

The specifics of the tested glaze, the *general expectations* to which it conforms and those to which it doesn't, the modifications to which it is exquisitely sensitive, and those that leave unchanged, these constitute the essence of the glaze. Any glaze can become the focal point of axis testing which, no doubt, will have a variety of results from awful to superb, but mostly just the basis for further tests.

Composition: Axis Test Glaze Family

The cone 10 glaze described below is fired in oxidation in an electric kiln. The kiln is a 2.6 cubic ft test kiln; an L&L JD18. The firing time from on to off is 18 hr 5 min. The firing has a 20-minute hold at peak temperature of 2310^{0}F. Orton cones report cone 10 down, and cone 11 tipped but not down.

The firing profile has a down fire with two slow ramps, from 1850^{0}F to 1700^{0}F at 50^{0}F/hour, and from 1700^{0}F to 1650^{0}F at 25^{0}F/hour. There are also two additional holds: a half hour at 1850^{0}F, and a 1 hour hold at 1650^{0}F.

The down fire part of this firing is shown in short form:
[1850 - 1700] at 50^{0}F an hour, 1/2 hr hold at 1850^{0}F
[1700 - 1650] at 25^{0}F an hour, 1 hr hold at 1650^{0}F

The ramp hold program is:

1. 150^{0}F hr/ 250^{0}F
2. 400^{0}F hr/ 2050^{0}F
3. 120^{0}F hr/ 2310^{0}F/ hold 20 min
4. 300^{0}F hr/ 1850^{0}F/ hold 1/2 hr
5. 50^{0}F hr/ 1700^{0}F
6. 25^{0}F hr/ 1650 deg F/ hold 1 hr

This is a high alkaline, saturated iron glaze that contains phosphorus. The glaze exhibits massed golden crystals and metallic luster. It has no tendency to drip, even when heavily applied. It 'stays' put so that it will hold surface decorations applied to the leather hard glaze. As stiff as it is, it doesn't easily crawl as is so common with low mobility glazes.

The empirical (or Seger) formula for this glaze is listed as Target in Table 1 opposite.

I measure the alkalinity of a glaze either as the ratio of alkali metals to other bases, or as the ratio of total alkali metals to alumina. The first of these measurements I call Alk:Other, and the second Alk:Alumina.

Herman Seger was the first to suggest that, as a measure of the alkalinity of a glaze .3 alkali metals was a 'good figure' for cone 10 glazes, giving a ratio of Alk:Other of .42.

Ideal Potash Feldspar has the chemical formula 1 K2O 1 Al2O3 6 SiO2, giving an Alk:Alumina ratio of 1. One can see from this that an Alk:Alumina ratio greater than 1 requires an alkali metal source, such as a frit or ash.

The glaze given above has an Alk-Alumina ratio of 1.56, which vastly exceeds the ideal potash feldspar value Alk:Alumina 1. It has an Alk:Other ratio of 3.5 which in turn greatly exceeds the Alk:Other ratio of .42 suggested by Hermann Seger.

For this reason. I consider the above glaze as the extreme-end achievable in the alkalinity of a ceramic glaze.

By both above measures, the glazes in The Axis Test Glaze Family, are high in alkali metals.

To be more specific regarding the ratios of this family of glazes, the left column is the name of the ratio, the next or middle column the lowest value for that ratio found, the last column is the highest value.

Silica:Alumina	5	7.25
Alk:Alumina (Alali metals:Alumina)	1.2	1.9
Alk:Other (Alkali metals:other Bases)	2.4	5.2

Each of these glazes differs (in its empirical formula) from the target or Ur glaze in one or two oxides. The difference is generally about 15%, though in some cases it is as high as 20%.

Table 1 shows each glaze's empirical formula.

The recipe for each glaze and images showing the results are given in the appendix.

General Findings

With only a dozen tests I found a substantial range of colors and textures. Colors varied from pale yellow to a deep burgundy that was almost indistinguishable from black. These glazes are multi-phase with variegated kaki reds containing microcrystals in an assortment of rainbow hues. Diverse surfaces included baby-butt mirror smooth gloss, and textured semi-matte. Metallic golden crystals ranged from a snow-like surface dusting to a dense cover through which the ground phase is invisible. Pewter-toned metallic crystals also are present.

The 12 glazes tested were variations of the glaze iron_8_Right_162_1Z_1. This glaze is seen in Figure 1.

I test individually for:

1. increase/decrease in silica
2. increase/decrease in alumina - this done in two increments
3. increase/decrease in fraction of base present - i.e. in increase of both silica and alumina. There are two increments for increase in both alumina and silica. Additionally, I increase in silica and alumina together with an increase in alkali metals.
4. increase/decrease in relative proportion of alkali metals in the glazes bases.

Table 2: The empirical (or Seger) formulas for the glaze family. *Target* is the Ur (target) glaze. Tests 1 to 12 are modifications to the base glaze.

Test #	Glaze	K_2O	Na_2O	Li_2O	CaO	MgO	BaO	SrO	ZnO	Al_2O_3	B_2O_3	Fe_2O_3	SiO_2	P_2O_5	ZrO_2	TiO_2
Base glaze:																
Target	satIron_ZG_H_1	.1010	.4907	.1908	.1561	.0614				.5032		.2007	3.1643	.04		.0011
Increase in alumina:																
1	satIron_ZG_0	.0994	.4904	.1944	.1564	.0593				.5936		.2048	3.1374	.0409		.0012
Larger increase in alumina:																
2	satIron_ZG_H_2	.1021	.5009	.2028	.1358	.0585				.6564		.2145	3.206	.0369		.0019
Decrease in alumina:																
3	satIron_ZG_1	.1002	.5011	.1867	.1703	.0418				.4395		.1960	3.1861	.0445		.0017
Further decrease in alumina:																
4	satIron_ZG_H_3	.1036	.4937	.1852	.1489	.0686				.4089		.1937	3.2132	.0441		.0004
Increase in silica:																
5	satIron_ZG_2	.0995	.4921	.2089	.1486	.0508				.5014		.1982	3.6634	.0373		.0089
Decrease in silica (and unavoidable shift in alkali metals):																
6	satIron_ZG_H_0	.0097	.4395	.3203	.1691	.0615				.5015		.1950	2.7423	.0451		.0041
Increase in both alumina and silica:																
7	satIron_ZG_4	.1015	.4971	.1834	.1543	.0637				.5593		.2016	3.5371	.0425		.0002
Additional increase in both alumina and silica:																
8	satIron_ZG_H_4	.1036	.4966	.1955	.1464	.0580				.6457		.2071	4.0071	.0398		.0004
Decrease in both alumina and silica (and unavoidable shift in alkali metals):																
9	satIron_ZG_H_1	.0104	.5237	.2310	.1701	.0648				.4610		.1953	2.917	.0450		.0027
Increase in ratio alkali metals: alkaline earths:																
10	satIron_ZG_6	.0700	.5302	.22376	.1383	.0239				.5593		.2002	3.1537	.0401		.0015
Decrease in ratio alkali metals: alkaline earths:																
11	satIron_ZG_7	.0596	.4506	.1928	.1900	.1071				.5003		.2060	3.1658	.0402		.0101
Increase in alumina and silica and alkali metals:																
12	satIron_ZG_H_5	.0096	.5137	.2251	.1381	.0235				.6329		.2045	4.0213	.0393		.0002
Test #	**Glaze**	**K_2O**	**Na_2O**	**Li_2O**	**CaO**	**MgO**	**BaO**	**SrO**	**ZnO**	**Al_2O_3**	**B_2O_3**	**Fe_2O_3**	**SiO_2**	**P_2O_5**	**ZrO_2**	**TiO_2**

All but the glaze with decreased alkali metal bases exhibited massed golden metallic crystals where glaze application was thick.

The changes seen with the above variations:

Following the Crystallieri, I describe the ground as the glaze in which no crystals have formed.

The background phase is a full gloss light brown to black glassy phase, which is not transparent but looks as if it might be.

This glaze varies greatly with changes in the ratio of alkali metals to alkaline bases, i.e. in the fraction of the basic oxides (fluxes) which are K2O/Na2O/Li2O.

The steepest change for this glaze is the alkali metal content.

Changes along the other axis are minimal. ■

About the Author

Carol Marians started with pottery in junior high school but majored in mathematics in college and went to graduate school at MIT with a National Science Foundation fellowship leading to her first Ph.D. in mathematics. But while a graduate student she also got her first potters wheel. Pottery and mathematics have been constant themes ever since. That includes a second MIT Ph.D. on Materials Science. With time spent working in the software industry and writing some of her own ceramics related programs, since "retiring" she has devoted her life to trying to understand the glazes she loves.

Appendix: Glaze recipes and images.

iron_8_R-162_1Z_1	Target
Bentonite	2
Bone Ash	4
Custer Feldspar	9
EPK Kaolin	6
Frit 413	27
Lithium Carbonate	4
Magnesium Carbonate	1
Nepheline Syenite	38
Red Iron Oxide	9
A 100 g batch has 0.283793 moles of base.	
Molecular percent Base	20.3455%
Molecular percent silica	64.3792%
Silica: Alumina ratio	6.28862
Alkali metal: Alumina ratio	1.55509

Increase in alumina:

satIron_ZG_0	Test 1
Bentonite	9
Bone Ash	10.5
EPK Kaolin	18
Frit 413	51
Lithium Carbonate	12
Nepheline Syenite	168
Red Iron Oxide	27
Talc	4.5
A 300 g batch of has 0.835392 moles of base.	
Molecular percent Base	20.0887%
Molecular percent silica	63.027%
Silica: Alumina ratio	5.28508
Alkali metal: Alumina ratio	1.32106

Further increase in alumina:

satIron_ZG_H_2	Test 2
Bone Ash	9
EPK Kaolin	18
Frit 413	51
Lithium Carbonate	12
Magnesium Carbonate	3
Nepheline Syenite	165
Red Iron Oxide	27
A 300 g batch has 0.800737 moles of base.	
Molecular percent Base	19.5476%
Molecular percent silica	62.6698%
Silica: Alumina ratio	4.88433
Alkali metal: Alumina ratio	1.22762

Decrease in alumina:

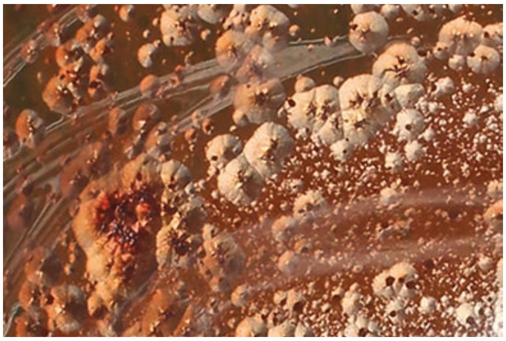
satIron_ZG_H_1	Test 3
Ball Clay	9
Bentonite	9
Bone Ash	12
Custer Feldspar	33
Dolomite	3
Frit 413	93
Lithium Carbonate	12
Nepheline Syenite	102
Red Iron Oxide	27
A 300 g batch has 0.870101 moles of base.	
Molecular percent Base	20.5427%
Molecular percent silica	65.4521%
Silica: Alumina ratio	7.24925
Alkali metal: Alumina ratio	1.79279

Further decrease in alumina:

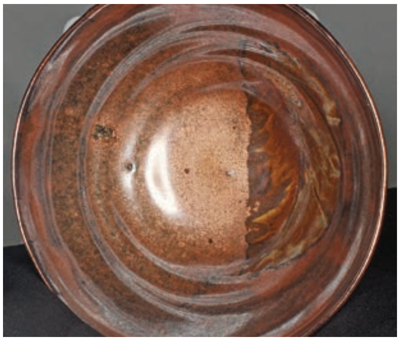
satIron_ZG_H_3	Test 4
Bentonite	18
Bone Ash	12
Custer Feldspar	45
Frit 413	99
Lithium Carbonate	12
Magnesium Carbonate	3
Nepheline Syenite	74
Red Iron Oxide	27
A 300 g batch has 0.877107 moles of base.	
Molecular percent Base	20.5751%
Molecular percent silica	66.111%
Silica: Alumina ratio	7.85869
Alkali metal: Alumina ratio	1.91368

General Material Information	
Nepheline Syenite mesh size	270
Silica mesh size	325
Bone Ash	natural
Custer Feldspar mesh size	325
Spodumene mesh size	200
EPK Kaolin mesh size	200

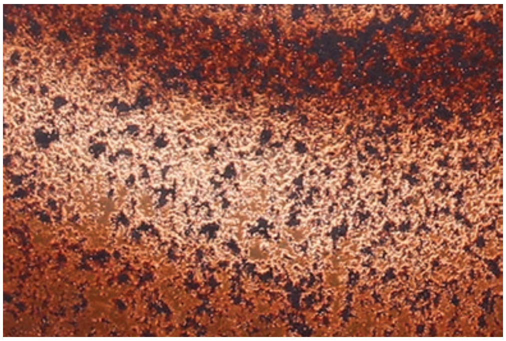
Target
The Ur (target) glaze iron_8_Right_162_1Z_1.



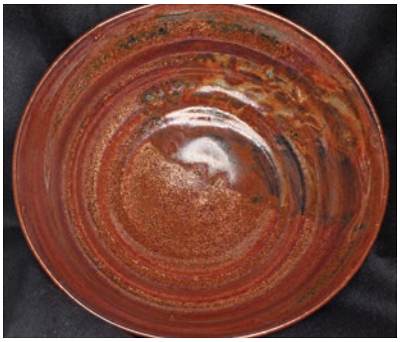
Test 1
Increase in Alumina. Glaze is satIron_ZG_0. Darker background, smaller denser metallic crystals, surface is waxy matte.

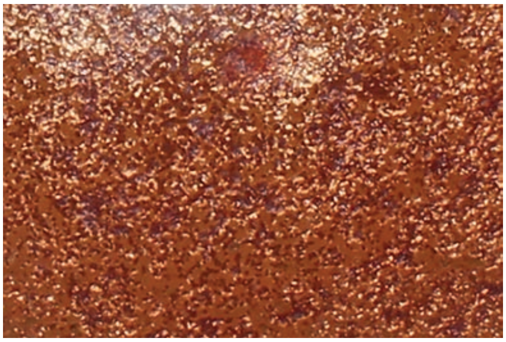


Test 2
Additional increase in Alumina. Glaze is satIron_ZG_H_2. Darker background and shift in hue toward purple, fewer crystals – though golden metallic crystals are present where glaze is thick.

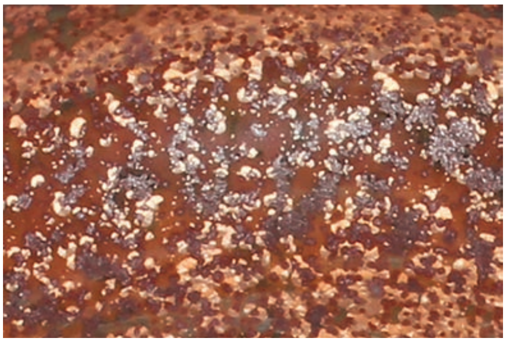


Test 3
Decrease in Alumina. Glaze is satIron_ZG_1. Lighter background, color shift to oranges and reds from burgundy seen in Test 2, a yellow tint appears. Surface shifts to full gloss.





Test 4
Additional decrease in Alumina. Glaze is satIron_ZG_H_3. Large brick red inclusions replacing much of the maroon seen in Test 2. Gold crystals are present and dense where glaze is thick.



Appendix continued ...

Increase in silica:

satIron_ZG_2	Test 5
Ball Clay	45
Bentonite	9
Bone Ash	9
Custer Feldspar	42
Dolomite	3
Frit 413	99
Lithium Carbonate	12
Nepheline Syenite	54
Red Iron Oxide	24
Silica	3
A 300 g batch has 0.77736 moles of base.	
Molecular percent Base	18.4871%
Molecular percent silica	67.725%
Silica: Alumina ratio	7.3058
Alkali metal: Alumina ratio	1.59658

Increase in both alumina and silica:

satIron_ZG_4	Test 7
Bentonite	9
Bone Ash	10.5
Frit 413	48
Lithium Carbonate	9
Magnesium Carbonate	3
Nepheline Syenite	165
Petalite	15
Red Iron Oxide	25.5
Silica	15
A 300 g has 0.797188 moles of base.	
Molecular percent Base	18.7245%
Molecular percent silica	66.2297%
Silica: Alumina ratio	6.32444
Alkali metal: Alumina ratio	1.39837

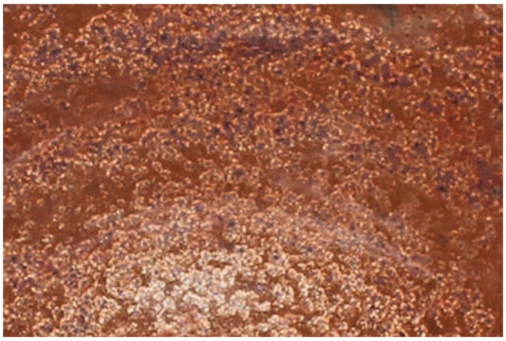
Decrease in silica
(and unavoidable shift in alkali metals[1]):

satIron_ZG_H_0	Test 6
Aluminium Hydroxide	9
Bone Ash	12
EPK Kaolin	78
Frit 413	135
Lithium Carbonate	21
Magnesium Carbonate	3
Nepheline Syenite	12
Red Iron Oxide	27
Whititng	3
A 300 g batch has 0.887375 moles of base.	
Molecular percent Base	22.2818%
Molecular percent silica	61.1044%
Silica: Alumina ratio	5.46834
Alkali metal: Alumina ratio	1.53435

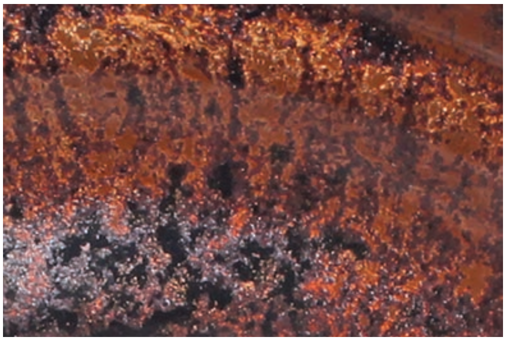
Additional increase in both alumina and silica:

satIron_ZG_H_4	Test 8
Bentonite	15
Bone Ash	9p
Custer Feldspar	27
Frit 413	75
Nepheline Syenite	84
Red Iron Oxide	24
Spodumene	63
Talc	3
A 300 g batch has 0.729198 moles of base.	
Molecular percent Base	16.7502%
Molecular percent silica	68.2925%
Silica: Alumina ratio	6.31457
Alkali metal: Alumina ratio	1.23223

Test 5
Increase in Silica.
Glaze is satIron_ZG_2.
Smaller metallic crystals, more uniform background color,increased surface gloss.

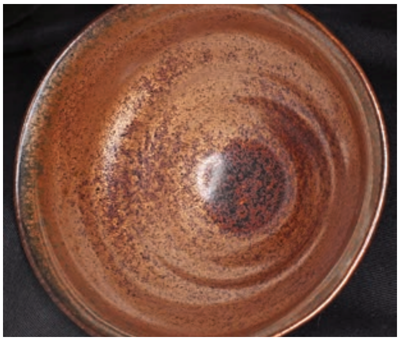


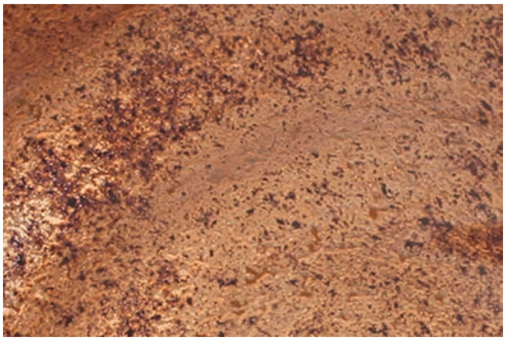
Test 6
Decrease in Silica.
Glaze is satIron_ZG_H_0.
Darker background color with a shift toward a burgundy tone. In addition to the predominant golden metallic crystals, redish metallic crystals are present. Surface texture is waxy. [1]



Test 7
Increase in both Alumina and Silica.
Glaze is satIron_ZG_4.
Glaze is glossier and background color lighter, crystal clusters are denser and smaller.

Test 8
Additional increase in both Alumina and Silica.
Glaze is satIron_ZG_H_4.
Background color shift even darker and browner, gold crystals are present and dense where glaze is thick. Glaze remains full gloss, gun metalcolored metallic crystals make an appearance.





Footnote
1. The confounding change, an unavoidable shift in the relative proportions of the alkali metals. The shift is the result of the computational limitation involved in creating a glaze recipe with a specified empirical formula.

Appendix continued ...

Decrease in both alumina and silica
(and unavoidable shift in alkali metals[1]):

satIron_ZG_H_1	Test 9
Aluminium Hydroxide	15
Bone Ash	12
EPK Kaolin	51
Frit 413	159
Lithium Carbonate	15
Magnesium Carbonate	3
Nepheline Syenite	15
Red Iron Oxide	27
Whiting	3
A 300 g batch has 0.878885 moles of base.	
Molecular percent Base	21.6395%
Molecular percent silica	63.1263%
Silica: Alumina ratio	6.32854
Alkali metal: Alumina ratio	1.6598

Decrease in ratio alkali metals: alkaline earths:

satIron_ZG_7	Test 11
Ball Clay	55.5
Bentonite	9
Bone Ash	10.5
Frit 413	84
Lithium Carbonate	12
Nepheline Syenite	90
Red Iron Oxide	27
Talc	9
Whiting	3
A 300 g batch has 0.842572 moles of base.	
Molecular percent Base	20.3159%
Molecular percent silica	64.3151%
Silica: Alumina ratio	6.32811
Alkali metal: Alumina ratio	1.40507

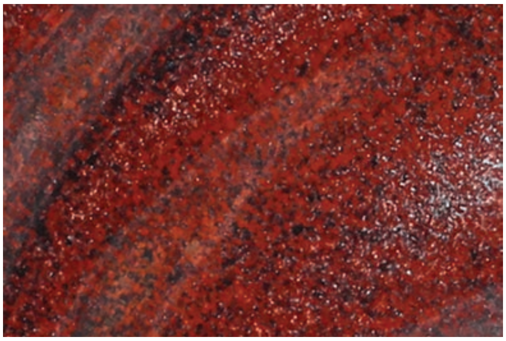
Increase in ratio alkali metals: alkaline earths:

satIron_ZG_6	Test 10
Bentonite	9
Bone Ash	10.5
EPK Kaolin	24
Frit 413	94.5
Lithium Carbonate	15
Nepheline Syenite	120
Red Iron Oxide	27
A 300 g batch has 0.854305 moles of base.	
Molecular percent Base	20.4054%
Molecular percent silica	64.3535%
Silica: Alumina ratio	6.2434
Alkali metal: Alumina ratio	1.6586

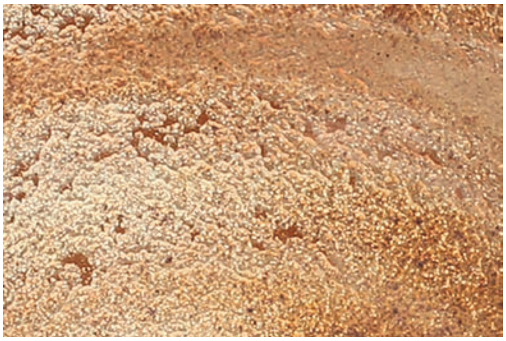
Increase in Alumina and Silica and Alkali metals:

satIron_ZG_H_5	Test 12
Bentonite	9
Bone Ash	9
Custer Feldspar	24
Frit 413	81
Lithium Carbonate	1.5
Nepheline Syenite	87
Red Iron Oxide	24
Spodumene	64.5
A 300 g batch has 0.738439 moles of base.	
Molecular percent Base	16.9544%
Molecular percent silica	68.1781%
Silica: Alumina ratio	6.35369
Alkali metal: Alumina ratio	1.32472

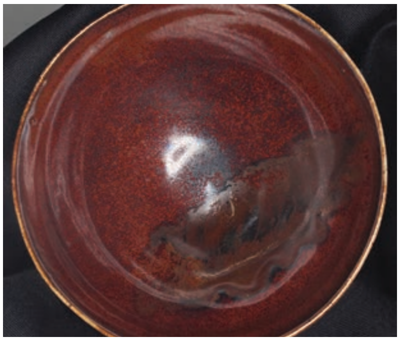
Test 9
Decrease in both alumina and silica. Glaze is satIron_ZG_H_1. Background color shift toward red, texture is lustrous waxy.[1]

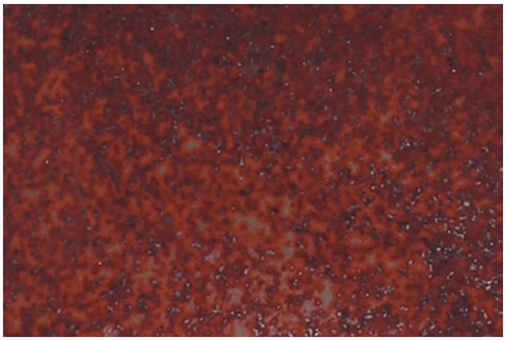


Test 10
Increase in the relative proportion of Alkali metal bases. Glaze is satIron_ZG_6. Color shift toward yellow, glossier glaze, substantial increase in metallic crystal density together with smaller crystals.

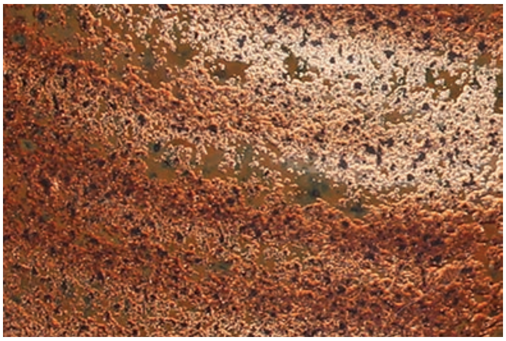


Test 11
Decrease in the relative proportion of Alkali metal bases. Glaze is satIron_ZG_7. Color is burgundy, crystals are nearly obliterated and are reduced to a glittery dusting so that the metallic nature of the crystals is not apparent. Surface is lustrous waxy.





Test 12
Increase in alumina and silica and alkali metals. Glaze is satIron_ZG_H_5. Color of background shifts darker, toward greenish black, larger crystal clusters which are denser. less background is visible, glossier surface.



Footnote
1. The confounding change, an unavoidable shift in the relative proportions of the alkali metals. The shift is the result of the computational limitation involved in creating a glaze recipe with a specified empirical formula.