

How do Glazes Work?

Eutectics
&
The Weight Percentage Formula

Part one

Eutectics

Why eutectics are important

How eutectics relate to everyday glazes

The Molecular Make-up of a Glaze

The difference between Moles and Weight Percentages

The inherent limits of the UMF method

Part two

The Weight Percentages Formula

Research findings

WPF Target Limits

WPF spread sheet calculation programs

&

Weight Percentage Diagram



Nigel Wood

Chinese Glazes

Lime Glazes > Lime Alkali Glazes

Lime eutectic

&

Percentage method

Some observations:

- The readiness to fuse is not determined by their molecular make-up of a glazes alone; ingredient choice and their particle size have a big impact as well
- Within all temperature ranges neither feldspar nor nepheline syenite help to obtain full fusion (low viscosity)
- A alumina silica ratio of 1 : 10 according to the UMF (high silica content relative to alumina) is generally assumed to be working well for shiny glazes. This is true for cone 10 feldspatic glazes and mid-range zinc glazes.
- Mid-and high range calcium glazes and for low- and mid-range calcium-boron glazes need a high alumina / kaolin content to yield shiny results.
- Silica matte glazes for cone 8 and beyond are more challenging to make stable
- In contrast to what often is stated; K_2O is much less of an active flux in glazes compared to Na_2O

Knowledge about eutectics in combination with the use of the Weight Percentage Formula will help to explain the underlying logic behind these observations.

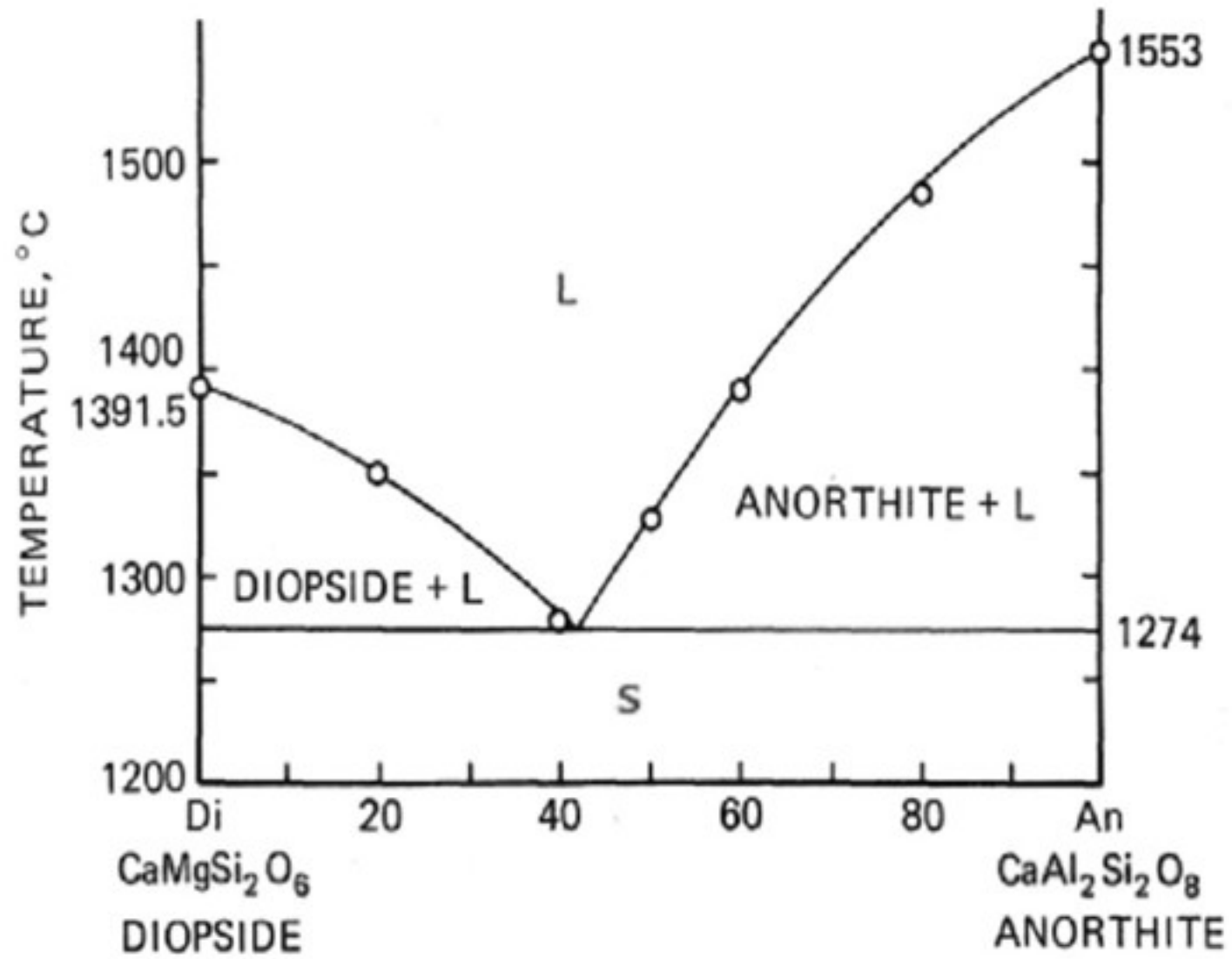
Eutectics

Eutectics

A eutectic reaction is a phenomenon in which a specific combination of oxides yields melting at a (considerable) lower temperature than that of each oxide individually

The exact composition and temperature at which a eutectic reaction occurs is determined under very specific and well controlled laboratory conditions

Binary Phase Diagrams



Trinary Phase Diagrams

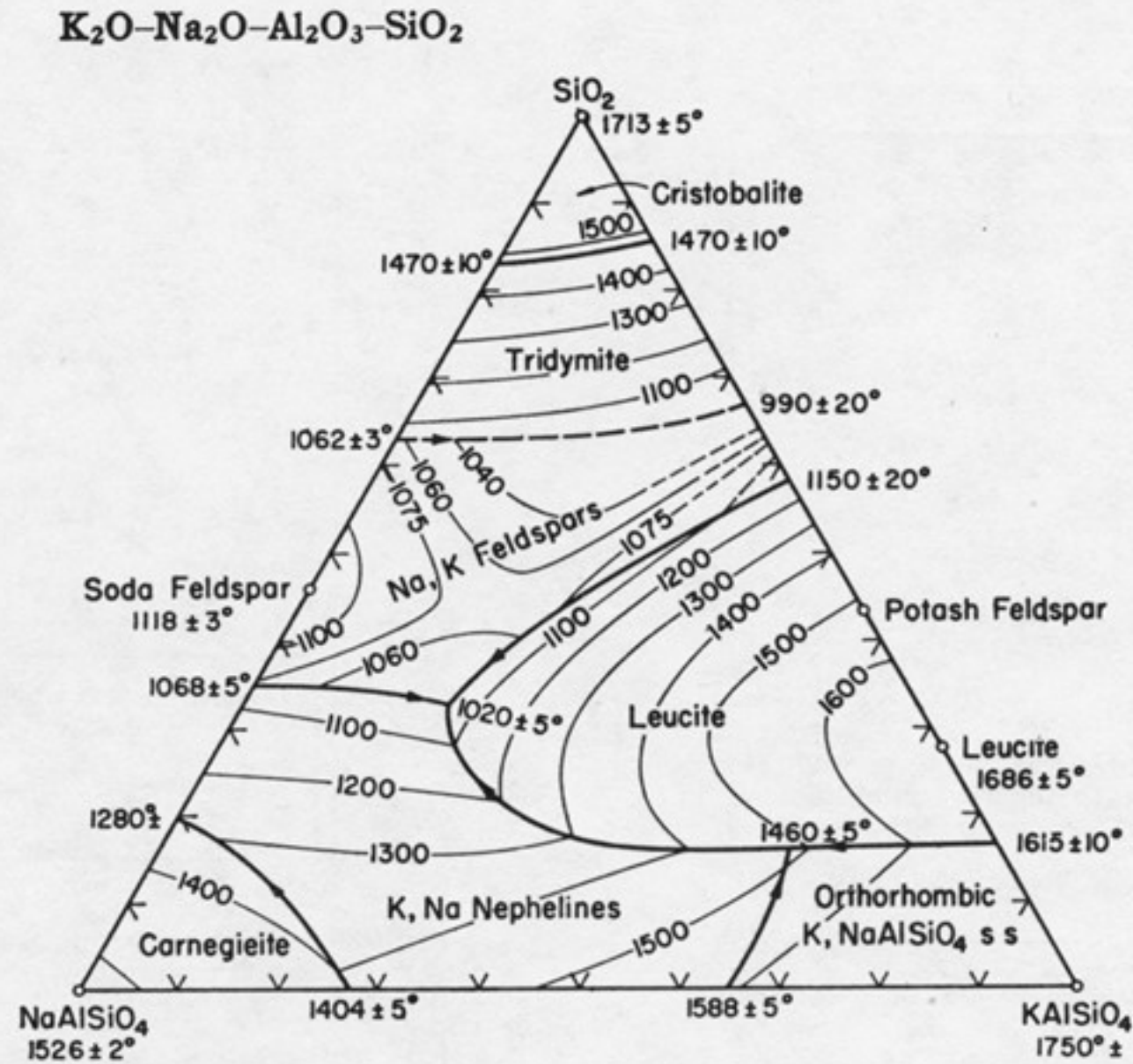


FIG. 786.—System $\text{NaAlSiO}_4-\text{KAlSiO}_4-\text{SiO}_2$; revised.

J. F. Schairer, *J. Geol.*, 58, No. 5, 514 (1950).

Why are Eutectics Important?

The melting behavior of glazes are largely determined by eutectics reactions; hence they are very helpful to understand and predict the nature of glazes.

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- the logic behind crystallization
- the influence of particle size on melting and crystallization
- the influence of surface tension on viscosity

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Glazes with a composition close towards a eutectic mixture tend to be shiny because they have less of a tendency to crystallize

But the influence of
eutectics reactions
on glazes
is...

But the influence of
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is
not
one to one!

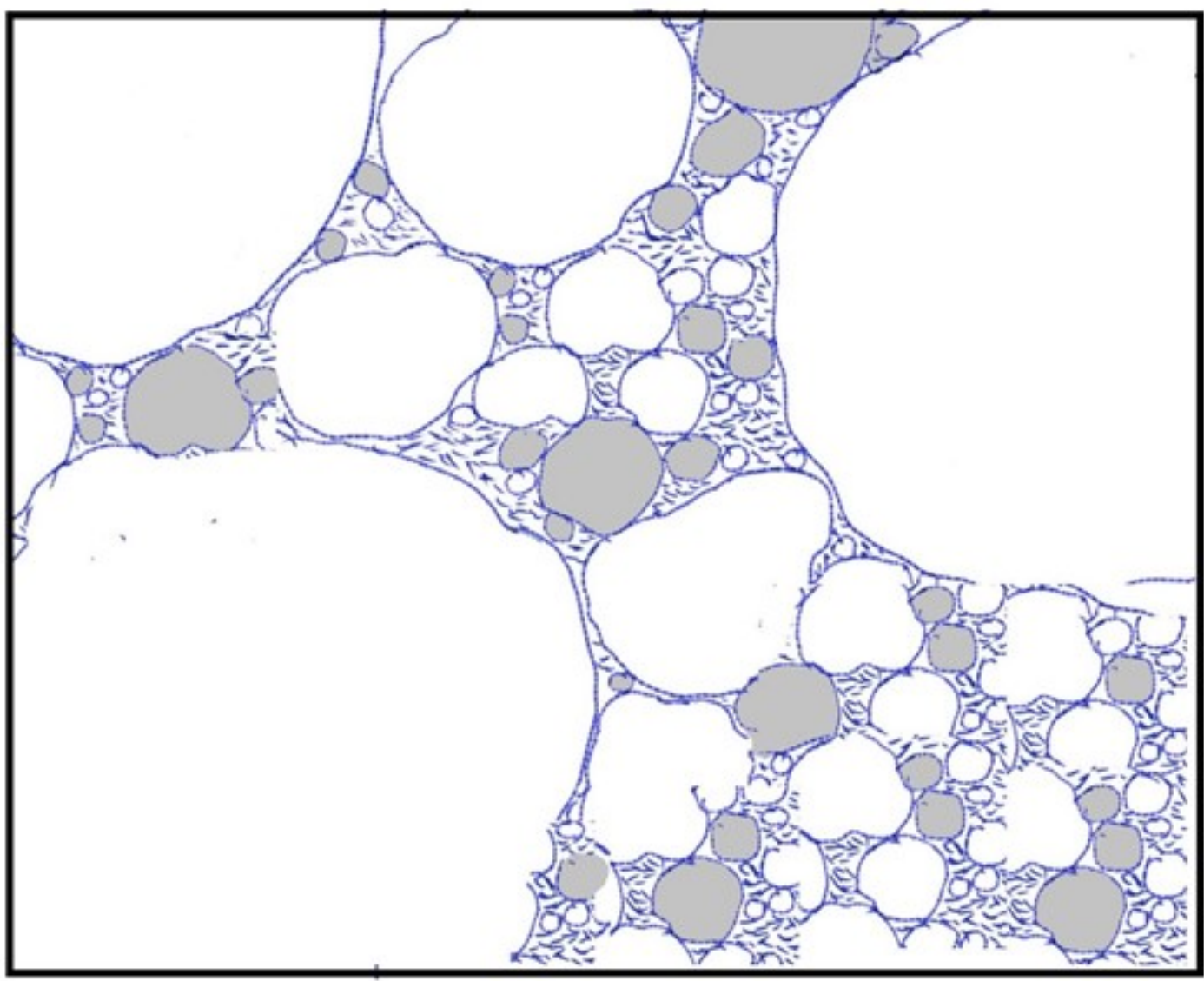
Eutectics and Glazes

There is a difference between the temperature at which a “eutectic glaze” will fuse and the related eutectic point. A differences of 50°C (122°F) but also as much as 500°C (932°F) or higher can occur because glazes consist of particles.

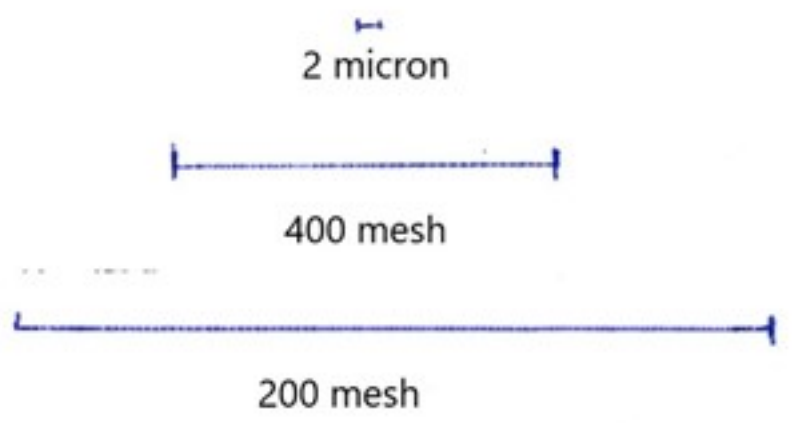
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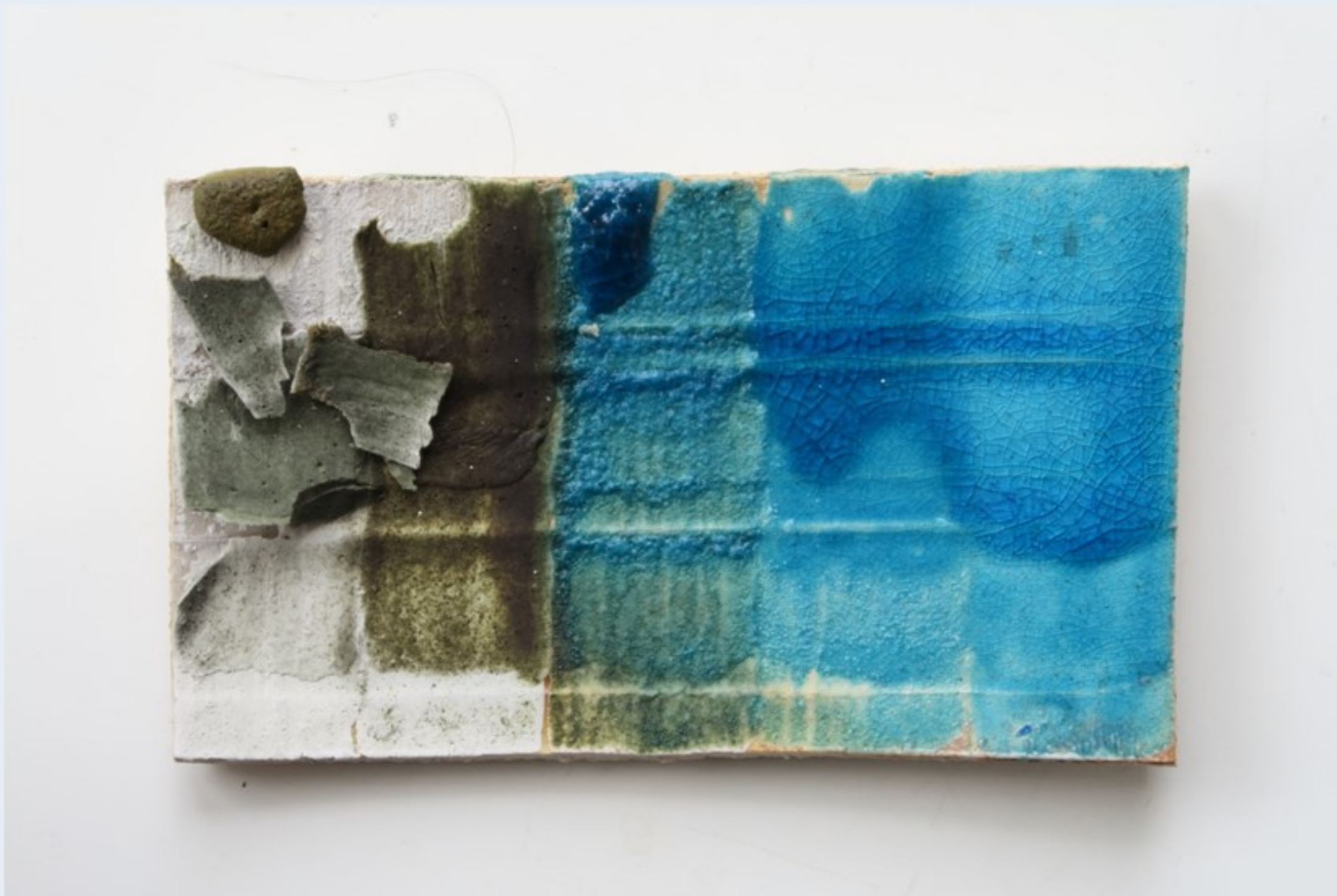
Particle will hamper a eutectic reaction to take place all over the glaze layer because initially molecules are only available at the surface of a particle. Hampering occurs even more so in case of larger particles and particularly in case high amount of refractory ingredients like quartz are involved.



1000 x enlarged



Average ingredient 75 - 2 microns
Clay minerals less than 2 microns



Cone 3

Potassium high silica eutectic
Eutectic point: 710°C (1310°F)

Sodium high silica eutectic
Eutectic point: 740°C (1364°F)

Mixture 1 (100% A)			Mixture 2 (75% A : 25% B)			Mixture 3 (50% A : 50% B)			Mixture 4 (25% A : 75% B)			Mixture 5 (100% B)		
Quartz Imsil A Alfred GEM	60,4	%	Quartz Imsil A Alfred GEM	57,8	%	Quartz Imsil A Alfred GEM	55,3	%	Quartz Imsil A Alfred GE	52,7	%	Quartz Imsil A Alfred GEM	50,2	%
Kaolin Grolleg A Alfred	9,3	%	Kaolin Grolleg A Alfred	9,0	%	Kaolin Grolleg A Alfred	8,6	%	Kaolin Grolleg A Alfred	8,3	%	Kaolin Grolleg A Alfred	8,0	%
Quartz Sil-co-sil (63) Gem	0,0	%	Quartz Sil-co-sil (63) Gem	0,0	%	Quartz Sil-co-sil (63) Gem	0,0	%	Quartz Sil-co-sil (63) Ge	0,0	%	Quartz Sil-co-sil (63) Gem	0,0	%
Neph. Sy. Spect. A Alfred	0,0	%	Neph. Sy. Spect. A Alfred	0,0	%	Neph. Sy. Spect. A Alfred	0,0	%	Neph. Sy. Spect. A Alfred	0,0	%	Neph. Sy. Spect. A Alfred	0,0	%
Minspar 200 A Alfred	0,0	%	Minspar 200 A Alfred	0,0	%	Minspar 200 A Alfred	0,0	%	Minspar 200 A Alfred	0,0	%	Minspar 200 A Alfred	0,0	%
P Feldspar Mahavir A Alfr	0,0	%	P Feldspar Mahavir A Alfr	0,0	%	P Feldspar Mahavir A Alfr	0,0	%	P Feldspar Mahavir A Al	0,0	%	P Feldspar Mahavir A Alfr	0,0	%
Whiting Cast Carb A Alfred	0,0	%	Whiting Cast Carb A Alfred	0,0	%	Whiting Cast Carb A Alfred	0,0	%	Whiting Cast Carb A Alfr	0,0	%	Whiting Cast Carb A Alfred	0,0	%
Dolomite Doloc A Alfred	0,0	%	Dolomite Doloc A Alfred	0,0	%	Dolomite Doloc A Alfred	0,0	%	Dolomite Doloc A Alfred	0,0	%	Dolomite Doloc A Alfred	0,0	%
Strontium Carb	0,0	%	Strontium Carb	0,0	%	Strontium Carb	0,0	%	Strontium Carb	0,0	%	Strontium Carb	0,0	%
Barium Carbonate	0,0	%	Barium Carbonate	0,0	%	Barium Carbonate	0,0	%	Barium Carbonate	0,0	%	Barium Carbonate	0,0	%
Pearl Ash K2CO3	30,3	%	Pearl Ash K2CO3	22,8	%	Pearl Ash K2CO3	15,2	%	Pearl Ash K2CO3	7,6	%	Pearl Ash K2CO3	0,0	%
Sodium Bicarb.	0,0	%	Sodium Bicarb.	10,5	%	Sodium Bicarb.	20,9	%	Sodium Bicarb.	31,4	%	Sodium Bicarb.	41,9	%
	100,0			100,0			100,0			100,0			100,0	

Eutectics and Glazes

Ingredients like feldspar or nepheline syenite increase the surface tension of a glaze considerably. If present in a eutectic glaze full fusion will be only obtained at a higher temperature because a high surface tension retards particles getting dissolved.

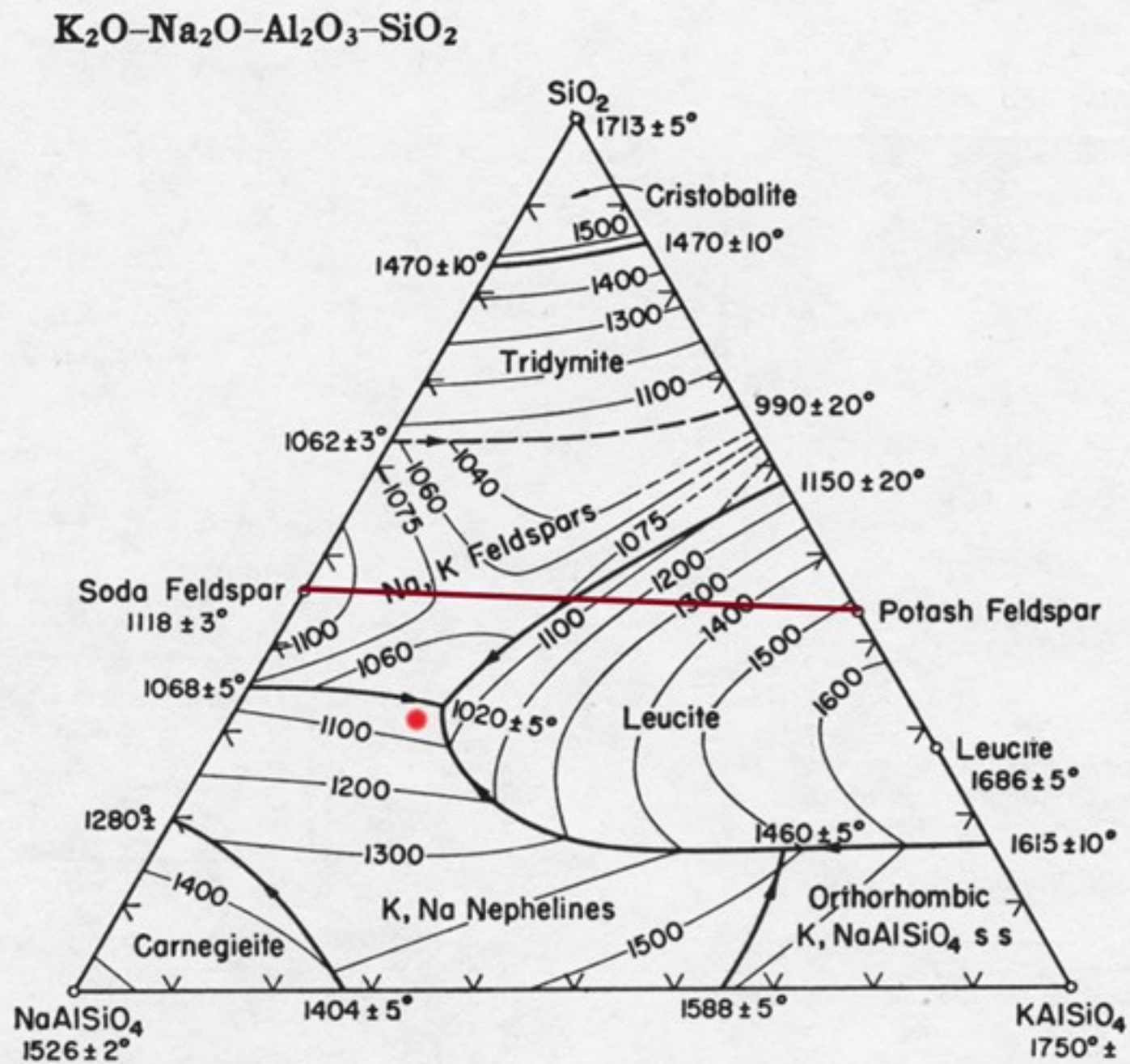


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Lime eutectic glaze – Nepheline syenite



Cone 5 and cone 7

Lime eutectic
Eutectic point: 1170°C (2138°F)

Sodium potassium high alumina eutectic
Eutectic point: 1020°C (1868°F)

Mixture 1 (100% A)	%	Mixture 2 (75% A : 25% B)	%	Mixture 3 (50% A : 50% B)	%	Mixture 4 (25% A : 75% B)	%	Mixture 5 (100% B) B	%
Quartz 400 mesh	34,9	Quartz 400 mesh	26,2	Quartz 400 mesh	17,5	Quartz 400 mesh	8,7	Quartz 400 mesh	0,0
Kaolin Grolleg A Alfred	32,3	Kaolin Grolleg A Alfred	24,3	Kaolin Grolleg A Alfred	16,2	Kaolin Grolleg A Alfred	8,1	Kaolin Grolleg A Alfred	0,0
Cal Kaolin Grolleg	0,0	Cal Kaolin Grolleg	0,0	Cal Kaolin Grolleg	0,0	Cal Kaolin Grolleg	0,0	Cal Kaolin Grolleg	0,0
Neph. Sy. Spect. A Alfred	0,0	Neph. Sy. Spect. A Alfred	25,0	Neph. Sy. Spect. A Alfred	50,0	Neph. Sy. Spect. A Alfred	75,0	Neph. Sy. Spect. A Alfred	100,0
Minspar 200 A Alfred	0,0	Minspar 200 A Alfred	0,0	Minspar 200 A Alfred	0,0	Minspar 200 A Alfred	0,0	Minspar 200 A Alfred	0,0
P Feldspar Mahvir A Alfr	0,0	P Feldspar Mahvir A Alfr	0,0	P Feldspar Mahvir A Alfr	0,0	P Feldspar Mahvir A Alfr	0,0	P Feldspar Mahvir A Alfr	0,0
Whiting Cast Carb A Alfred	32,7	Whiting Cast Carb A Alfred	24,6	Whiting Cast Carb A Alfred	16,4	Whiting Cast Carb A Alfred	8,2	Whiting Cast Carb A Alfred	0,0
Dolomite Doloc A Alfred	0,0	Dolomite Doloc A Alfred	0,0	Dolomite Doloc A Alfred	0,0	Dolomite Doloc A Alfred	0,0	Dolomite Doloc A Alfred	0,0
Wollastonite Vansil A Alfr	0,0	Wollastonite Vansil A Alfr	0,0	Wollastonite Vansil A Alfr	0,0	Wollastonite Vansil A Alfr	0,0	Wollastonite Vansil A Alfr	0,0
Talc	0,0	Talc	0,0	Talc	0,0	Talc	0,0	Talc	0,0
Frit 3134 (High Bo and So)	0,0	Frit 3134 (High Bo and So)	0,0	Frit 3134 (High Bo and So)	0,0	Frit 3134 (High Bo and So)	0,0	Frit 3134 (High Bo and So)	0,0
Sodium Bicarb.	0,0	Sodium Bicarb.	0,0	Sodium Bicarb.	0,0	Sodium Bicarb.	0,0	Sodium Bicarb.	0,0
	100,0		100,0		100,0		100,0		100,0

Eutectics and Glazes

Despite being less subjected to crystallization a “eutectic glaze” still can turn matte. Crystals are formed during firing as a result of an exchange of molecules between particles. These crystals, as well as not fully dissolved particles, will form seeds for crystal growth during cooling.

The tendency of this to occur increases if ingredients with a coarser particle size are used

Eutectics and Glazes

Eutectic mixtures can be used as **reference points** within an infinite amount of possible compositions.

The Molecular Make-up of a Glaze

Moles versus Weight Percentages

Moles

The standard method for denoting the molecular make-up of glazes and crystals

Is a counting unit for molecules based on the Avogadro constant; one Mole contains 6.02×10^{23} molecules

It is a way to express very large numbers in chewable chunks like 3,153,600,00 seconds can be expressed as being 1 century

$$\frac{\text{Gram or \% of oxide}}{\text{Molecular Mass of oxide}} = \text{Mole}$$

The relative molecular mass (MM) is the mass of an atom or molecule in relation to a standard value. Historically the standard value was the smallest atom: H (Hydrogen)

The Unity Molecular Formula

UMF		
R_2O	R_2O_3	RO_2
RO		
1	$Al_2O_3 : SiO_2$	

Moles Versus Weight Percentages

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Note! Do not confuse weight percentages and Mole percentages!

Moles Versus Weight

100g of alumina = **0.98 Moles**

$$\frac{100}{102} = 0.98$$

100g of silica = **1.66 Moles**

$$\frac{100}{60.1} = 1.66$$

Moles Versus Weight

1 kg of apples or 1 kg of walnuts
will contain a different number of apples or walnuts

Making a pie:

counting the individual components

< >

weighing the component

Moles Versus Weight Percentages

By using the UMF the relationship between the recipe and the molecular makeup of the final glaze becomes blurred because

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As a result it is more difficult to understand how glazes work

The limitations of the UMF method becomes apparent if a weight percentages approach to glaze calculation is used

The Weight Percentage Formula

addition

or

alternative to the UMF?

UMF

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- the relationship between a recipe and the molecular makeup of a glaze becomes blurred
- less clarity will be obtained when comparing different type of glazes
- it is not possible to make more detailed distinctions between glaze types.

The Weight Percentage Formula

WPF		
% K_2O % Na_2O	KNaO	
% CaO % MgO % ZnO % SrO % BaO % PbO % B_2O_3	% Al_2O_3	% SiO_2 % P_2O_5
Total fluxes	$Al_2O_3 : SiO_2$ <hr style="border-top: 1px dotted black;"/> KNaO : CaO	

UMF versus WPF

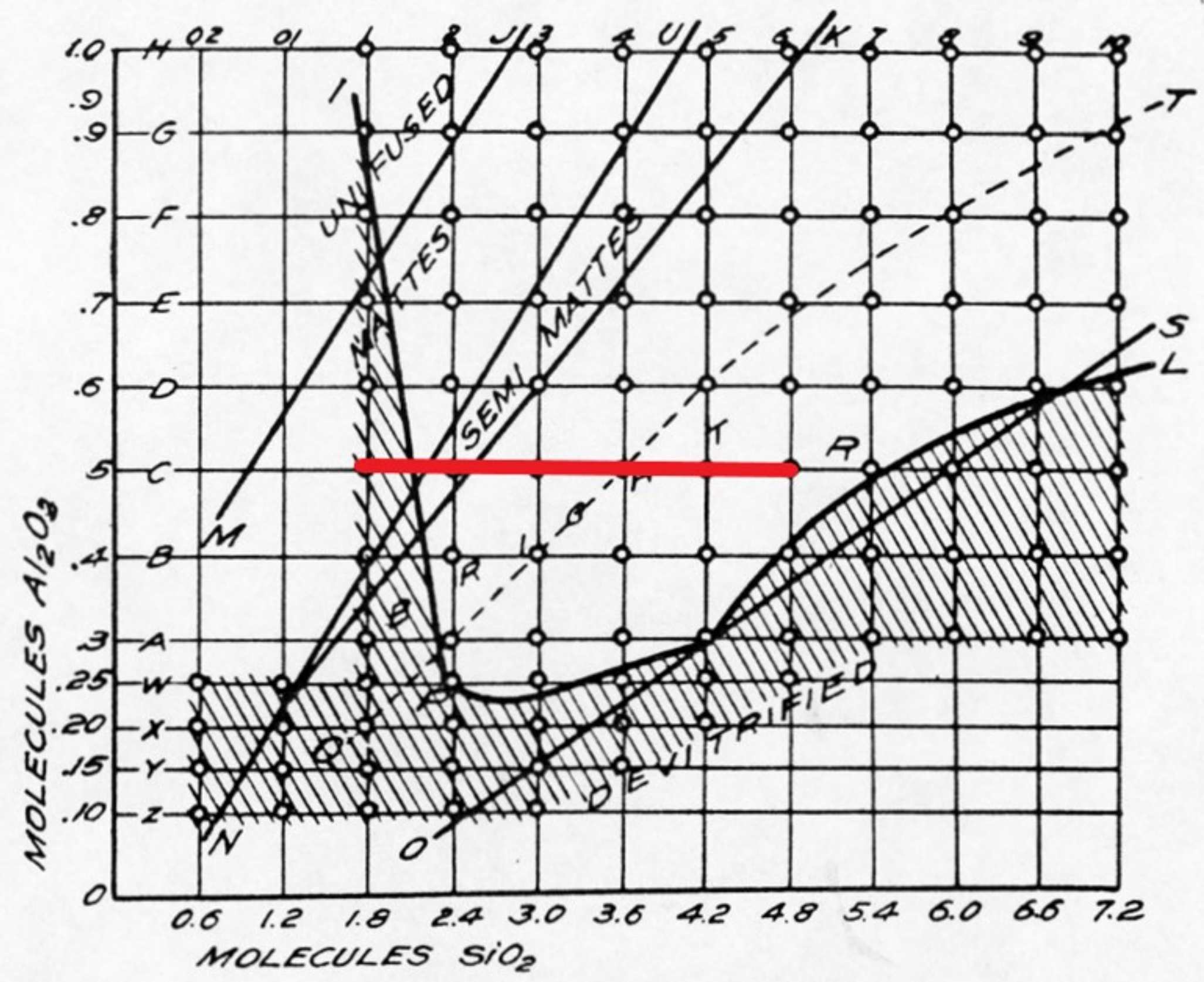
Two examples

Recipe		
Quartz	35%	35%
Neph. Sy.	40%	40%
Whiting	25%	-
Barium carb.	-	25%
WPF		
KNaO	7.2%	6.8%
CaO	15.7%	0.3%
MgO	0.1%	0.1%
BaO	-	20.7%
Total fluxes:	23.1%	27.9%
Al ₂ O ₃	10.6%	9.9%
SiO ₂	66.3%	62.3%
UMF		
KNaO	0.27	0.44
CaO	0.72	0.12
MgO	0.01	0.09
BaO	-	0.35
Fluxes:	1	1
Al ₂ O ₃	0.27	0.40
SiO ₂	2.85	4.31

MM:

CaO = 56.1

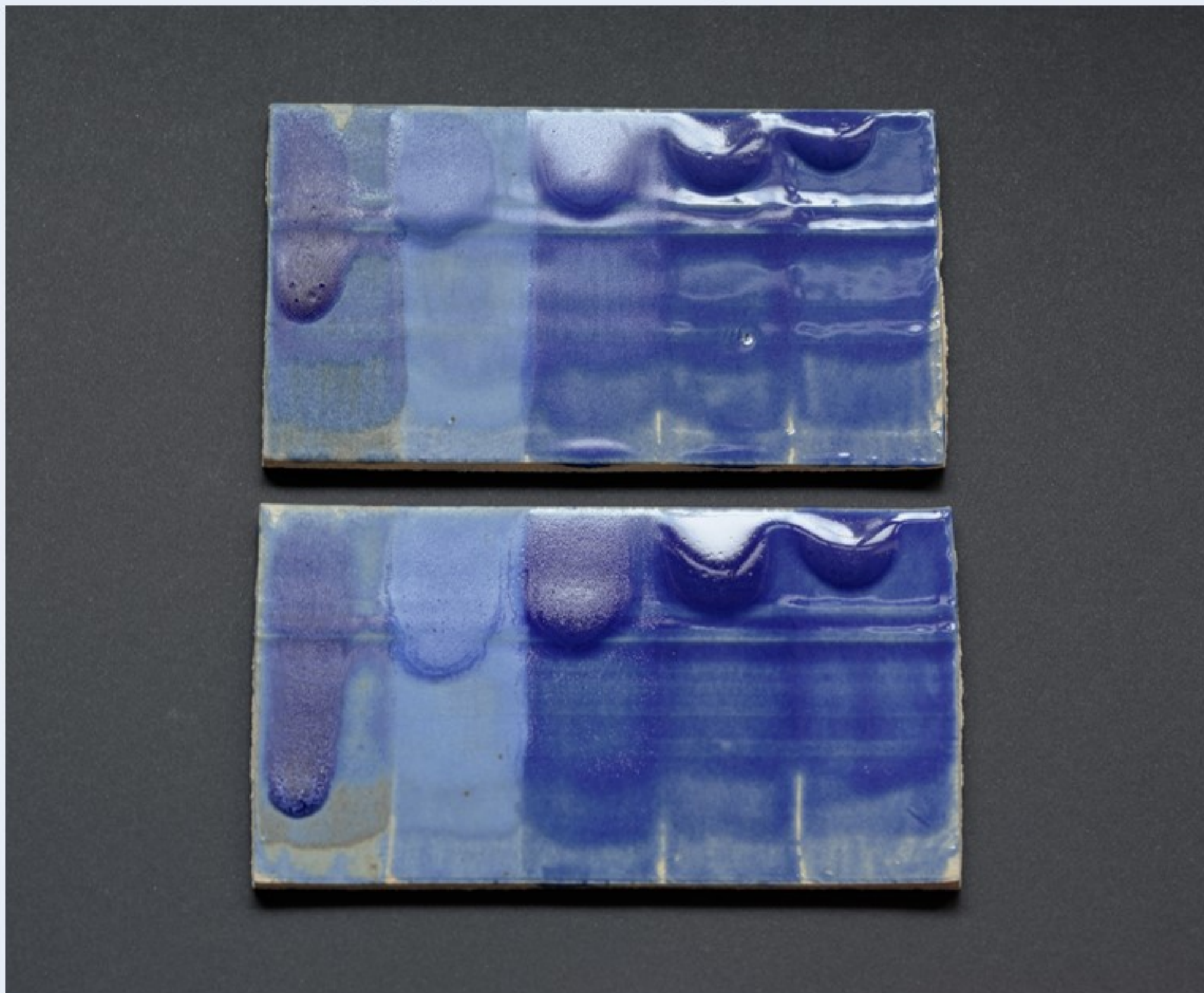
BaO = 153.7



0.5 Alumina 1.8 - 4.8 Silica

	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5					
Quartz	1.3	11.7	22.0	32.3	42.6					
Kaolin	22.6	20.4	18.2	16.1	13.9					
Neph. Sy.	49.1	43.8	38.5	33.2	27.9					
Whiting	27	24.1	21.3	18.5	15.6					
UMF:		Fluxes		Fluxes		Fluxes		Fluxes		Fluxes
KNaO	0.3		0.3		0.3		0.3		0.3	
CaO	0.7	1	0.7	1	0.7	1	0.7	1	0.7	1
Al ₂ O ₃	0.5		0.5		0.5		0.5		0.5	
SiO ₂	1.8		2.3		2.9		3.7		4.8	
WPF:		Fluxes		Fluxes		Fluxes		Fluxes		Fluxes
KNaO	9.7%		8.5%		7.3%		6.2%		5.2%	
CaO	17.7%	27.5%	15.7%	24.2%	13.7%	21.0%	11.7%	18.0%	9.8%	15.0%
Al ₂ O ₃	23.2%		20.5%		17.8%		15.3%		12.8%	
SiO ₂	49.3%		55.3%		61.1%		66.8%		72.2%	

Stull 0.5 Al₂O₃ 1.8 – 4.8 SiO₂ cone 7 and cone 9



Why bother?

The WPF approach allows to generate target limits with higher precision and application value and as such better predict the nature of a glaze

On top of that research has shown:

- A clear link between the total flux content and the optimal firing temperature of a glaze

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 - Increases durability (particularly surface hardness)
 - Reduces the chance of glaze stains to destabilize
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 - crystallization
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 - the range of glaze compositions that will melt between cone 4 and 7, but also below cone 4
- The KNaO % in relation to the KNaO : CaO ratio allows to predict the degree of crystallization and as such whether a stable shiny or matte glaze will be obtained

WPF Target Limits

WPF Target Limits for Stable Shiny Calcium Glazes Cone 4 - 10								Best results:
Cone	Total Flux*	KNaO **	CaO		B ₂ O ₃	MgO	Al ₂ O ₃ : SiO ₂	High Durability: 23% fluxes or less. Not more than 6% KNaO, 3% or less works better
4	28 – 25%	2 - 3%	Various amounts	0 - 5% ZnO, SrO or BaO to the expense of CaO	5 - 6%	1 -2%	1 : 4 - 1 : 4.2	Glaze stain stability: Not more than 6% KNaO, 3% or less works better
5	26 - 23%	2 - 3%			4 - 5%	1 -2%	1 : 4 - 1 : 4.2	
6	25 - 22%	2 - 3%			2 - 3%	1 -2%	1 : 4 - 1 : 4.2	400 mesh quartz and whiting
7	24 - 20%	2 - 4%			0 - 1%	1 - 2.4%	1 : 4.2 - 1 : 5	cone 4 - 9 (10) nepheline syenite
8	22 - 19%	3 -5%			0%	1 - 2%	1: 4.4 - 1: 5.5	cone 7 - 10 sodium feldspar
9	21 - 18%	3 - 6%			0%	1 - 1.5%	1 : 4.6 - 1: 6	cone 9 – 10 potash feldspar
10	20 – 17%	3 - 6%			0%	1 - 1.5%	1 : 4.8 - 1: 7	Up to 25% kaolin for biscuit in combination with CMC gum

* Less fluxes are needed in case of an increasing amount of Li₂O, CuO, MnO₂, FeO, Fe₂O₃, TiO₂, CoO

** Type of glazes: 1 – 3.5% KNaO Lime Glazes

3.5 – 8% KNaO Lime-Alkali Glazes

WPF Target Limits for Stable Shiny Zinc Glazes Cone 3 - 5								Best results:
Cone	Total Flux*	KNaO **	ZnO	CaO	B ₂ O ₃	MgO	Al ₂ O ₃ : SiO ₂	High Durability: 23% fluxes or less. Not more than 6% KNaO, 3% or less works better
3	26 - 24%	6- 7%	8 - 10%	Various amounts	?	1 %	1 : 6 - 1 : 6.5	Glaze stain stability: Not more than 6% KNaO, 3% or less works better
4	25 - 23%	6 -7%	6 - 8%		?	1 %	1 : 6 - 1 : 6.5	400 mesh quartz and whiting
5	24 - 21%	6 - 7%	4 - 6%		?	1 %	1 : 6 - 1 : 6.5	Nepheline syenite

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** Type of glazes: 3.5 – 8% KNaO Zinc-Alkali Glazes

WPF Target Limits for <u>Stable Calcium Alumina Matte Glazes</u> Cone 4 - 10						Best results:		
Cone	Total Flux*	KNaO**	CaO	B ₂ O ₃	Al ₂ O ₃ : SiO ₂			
4	31 – 27%	3-9%	Various amounts	2 - 4%	1 : 3	High Durability: 23% fluxes or less. Not more than 6% KNaO, 3% or less works better		
5	30 - 26%			1 -3%		Glaze stain stability: Not more than 6% KNaO, 3% or less works better		
6	29 - 25%			0 - 2%		325 - 400 mesh quartz and whiting		
7	28 - 23%			0 - 1%		cone 4 - 9 (10) nepheline syenite		
8	26 - 22%	3 - 7%		0%	1 : 3	cone 5 - 10 MS 200		
9	23– 21%			0%		cone 6 – 10 potash feldspar		
10	22 – 20%			0%				Up to 25% kaolin for biscuit in combination with CMC gum

* Less fluxes are needed in case of an increasing amount of Li₂O, CuO, MnO₂, FeO, Fe₂O₃, TiO₂, CoO

** Type of glazes: 1 – 3.5% KNaO Lime Glazes
3.5 – 8% KNaO Lime-Alkali Glazes
8 – 10% KNaO Alkali-Lime Glazes

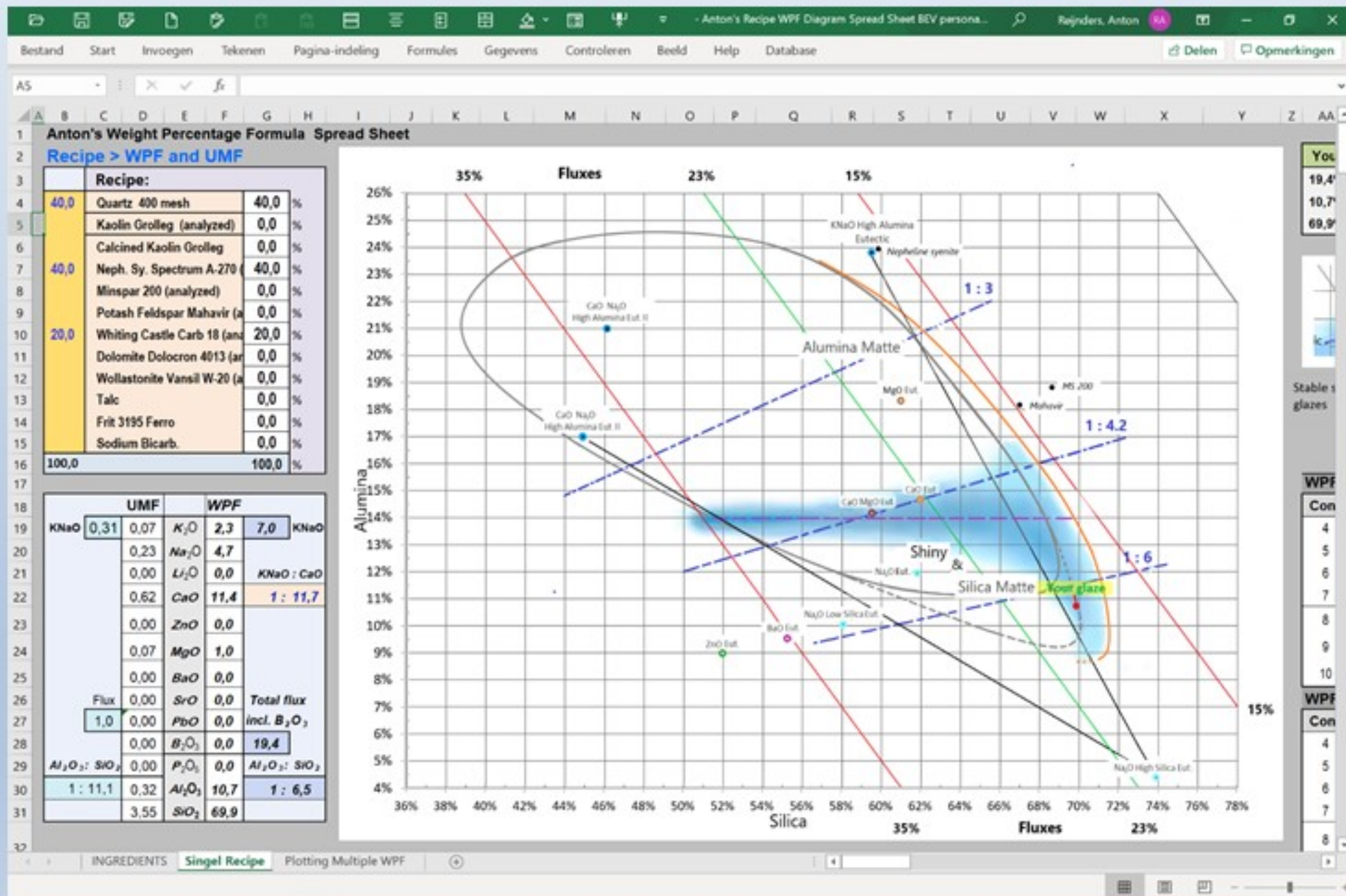
WPF Target Limits for <u>Calcium Silica Matte</u> Glazes Cone 4 - 10						Best results:
Cone	Total Flux*	KNaO **	CaO	B ₂ O ₃	Al ₂ O ₃ : SiO ₂	
4	31 - 27%	3-9%	Various amounts	2 - 4%	1 : 5	High Durability: 23% fluxes or less. Not more than 6% KNaO, 3% or less works better
5	30 - 26%			1 - 3%	1 : 5	Glaze stain stability: Not more than 6% KNaO, 3% or less works better
6	29 - 25%			0 - 2%	1 : 5	325 - 400 mesh quartz and whiting
7	28 - 23%			0 - 1%	1 : 6	cone 4 - 9 (10) nepheline syenite
8	26 - 22%	3 - 7%		0%	1 : 7	cone 5 - 10 MS 200
9	23 - 21%			0%	1 : 9	cone 6 - 10 potash feldspar
10	22 - 20%			0%	1 : 10	Up to 25% kaolin for biscuit in combination with CMC gum

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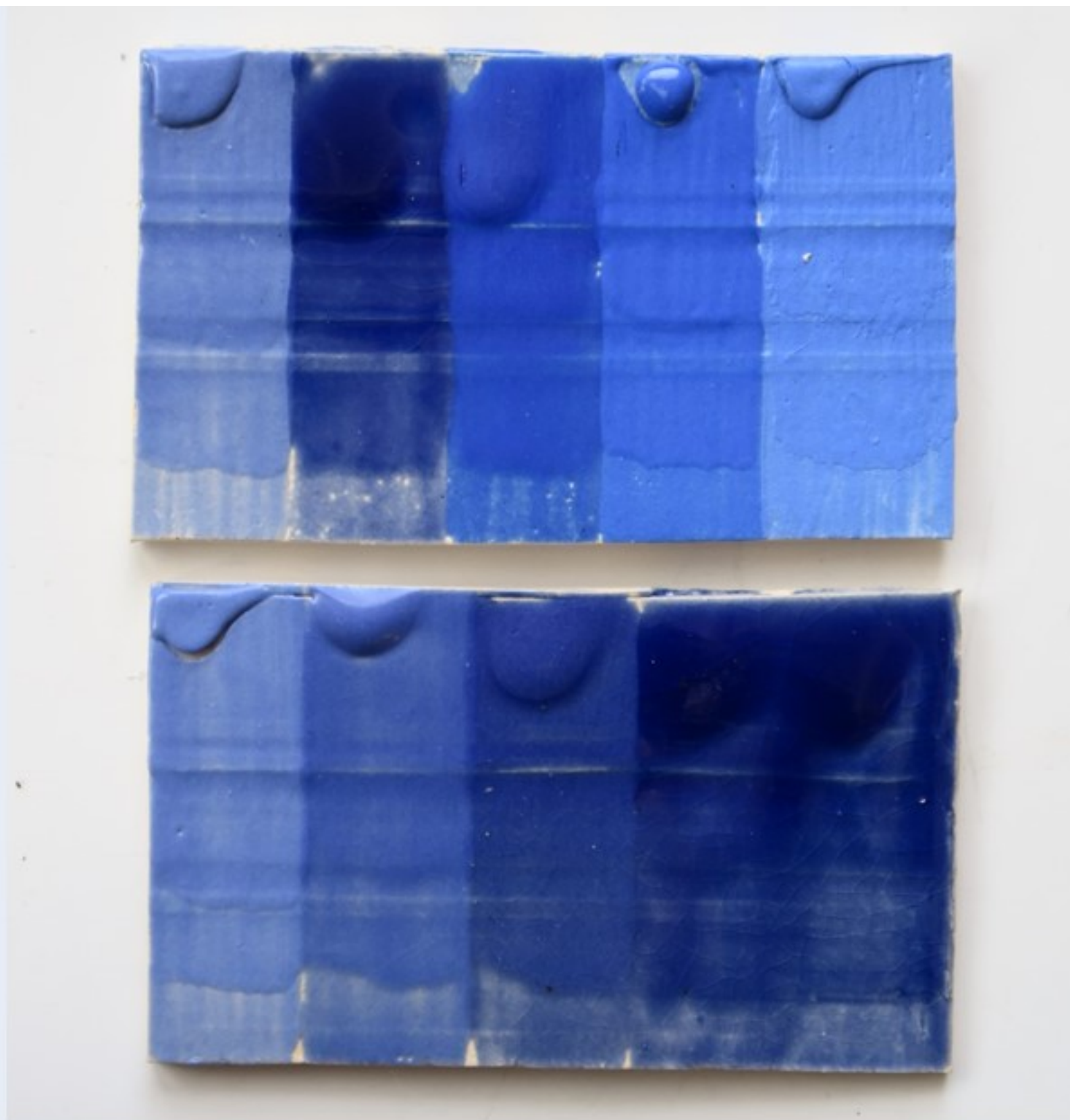
Low Crystallization Rate	
KNaO	KNaO : CaO
1%	1 : 22
2%	1 : 10
2.5%	1 : 7.1
3%	1 : 5.5
3.5%	1 : 4.4
4%	1 : 3.6
4.5%	1 : 2.9
5%	1 : 2.4
5.5%	1 : 2
6%	1 : 1.7
7%	1 : 1.3

WPF Glaze Calculation Spread Sheet & WPF Diagram



Observations:

- The readiness to fuse is not determined by their molecular make-up of a glazes alone; ingredient choice and their particle size have a big impact as well
- Within all temperature ranges neither feldspar nor nepheline syenite help to obtain full fusion (low viscosity)
- **An alumina-silica ratio of 1 : 6.2 (1 : 10 according to the UMF) is generally assumed to be working well for shiny glazes. This is true for cone 10 feldspatic glazes and mid-range zinc glazes**
- Mid-and high range Lime glazes and low- and mid-range calcium-boron glazes need a relative high alumina / kaolin content to turn shiny
- Silica matte glazes for cone 8 and beyond are more challenging to make stable



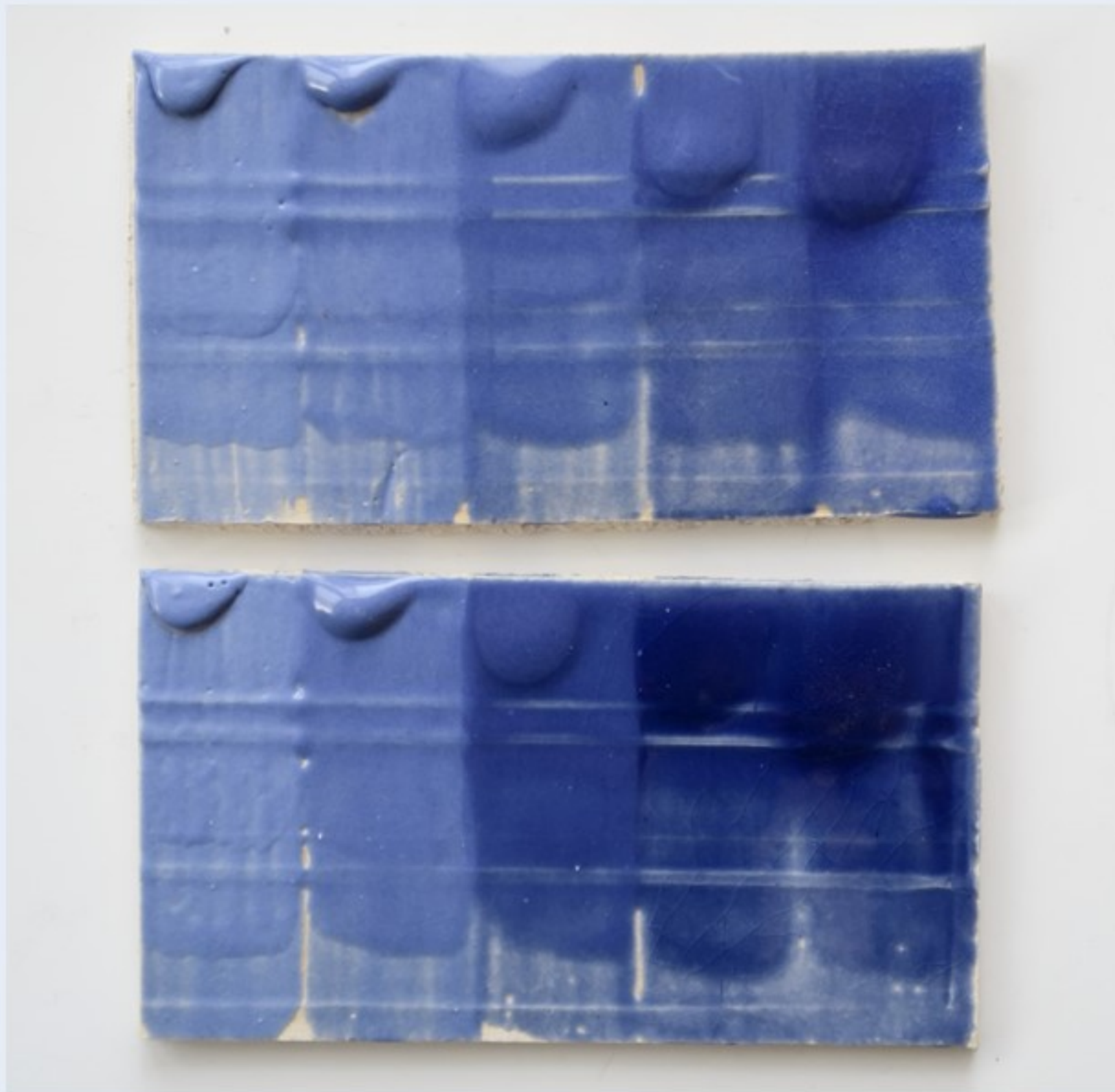
Cone 4

40 - 40 - 20 - Quartz + ZnO

40 - 40 - 20 - Quartz + ZnO 9%

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Cone 4

40 - 40 - 20 + Fr 3124

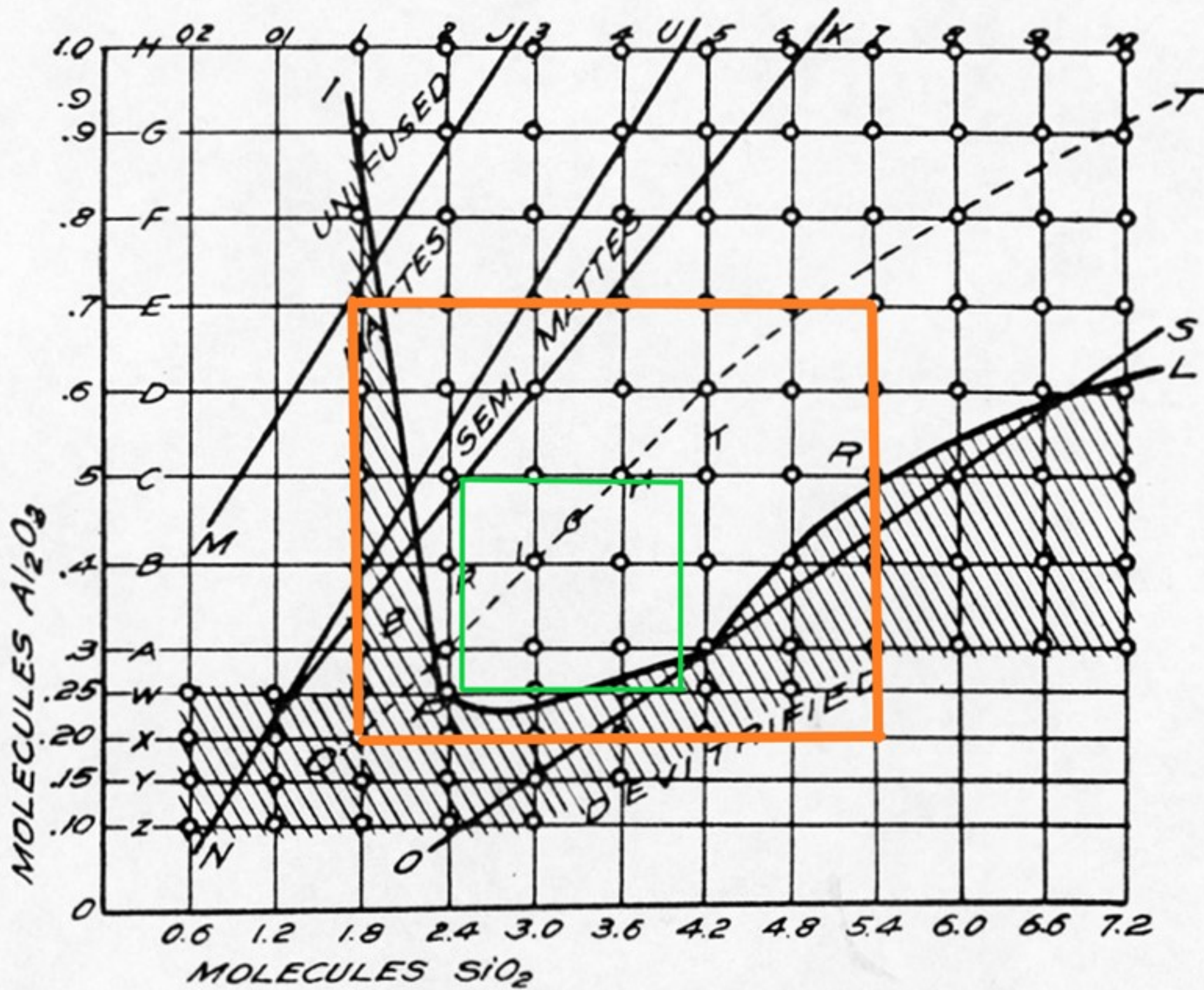
40 - 40 - 20 + Fr 3124 + Kaolin - Quartz

Observations:

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Stull: 0.3 KNaO 0.7 CaO 0.2 – 0.7 Al₂O₃ 1.8 – 5.4 SiO₂

