

How Glazes Melt



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NCECA · 2012

On the Edge

Seattle, Washington

Firing Temperatures?

Cone 10?

Broad range of melting compositions

Low Fire?

Naturally occurring, contaminated clays
(body considerations)

Mid-range?

Energy savings

Body density

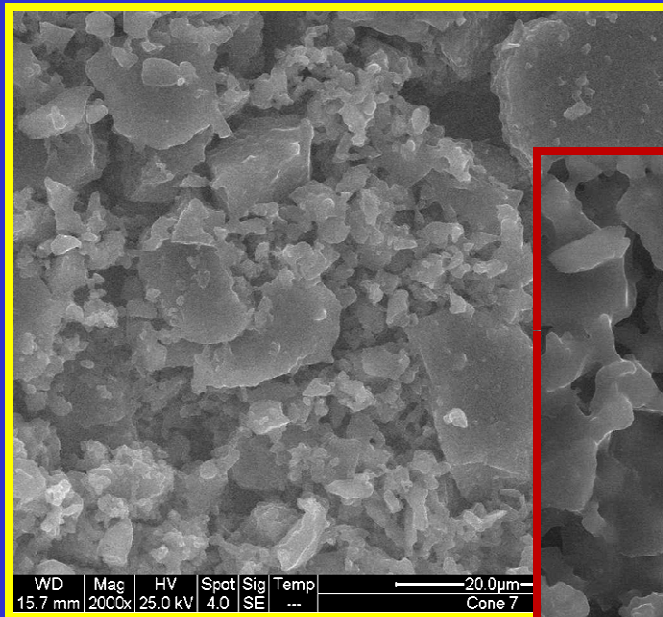
Glaze durability

How do Glazes Melt?

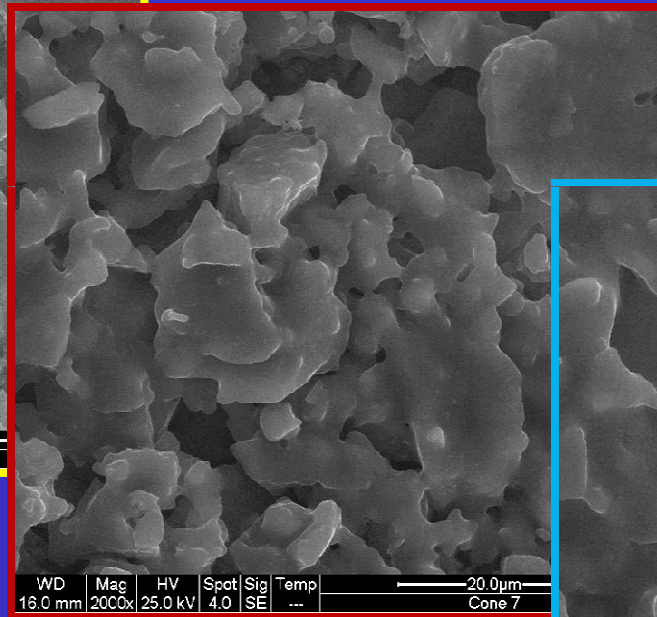
Pyrometric cones give us insight

Understanding
melting reactions
reveals a lot
about glazes.

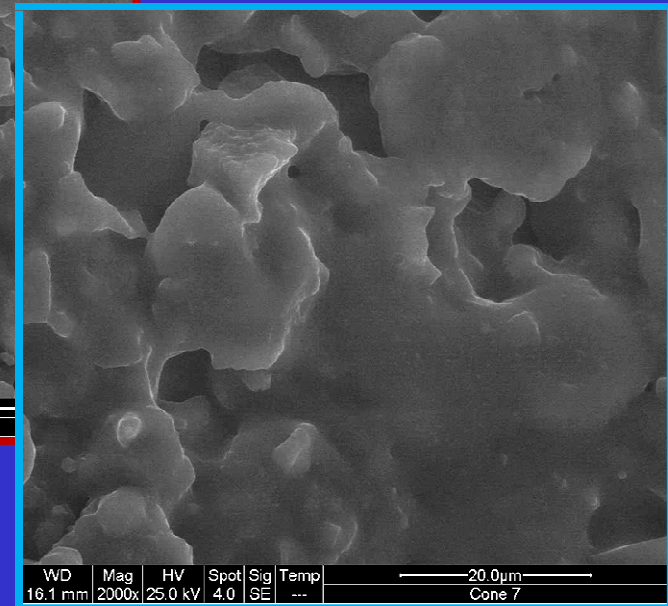
800°C



1200°C



1300°C



SEM images of *in situ* melting of a $\Delta 7$
pyrometric cone.

Courtesy: Dr. Tom Lam.

What is a Eutectic?

Eutectic temperature

The lowest temperature at which a given combination of elements will melt.

Heat = Melting

DETAILS: How Raw Glazes Melt

Melting takes time.

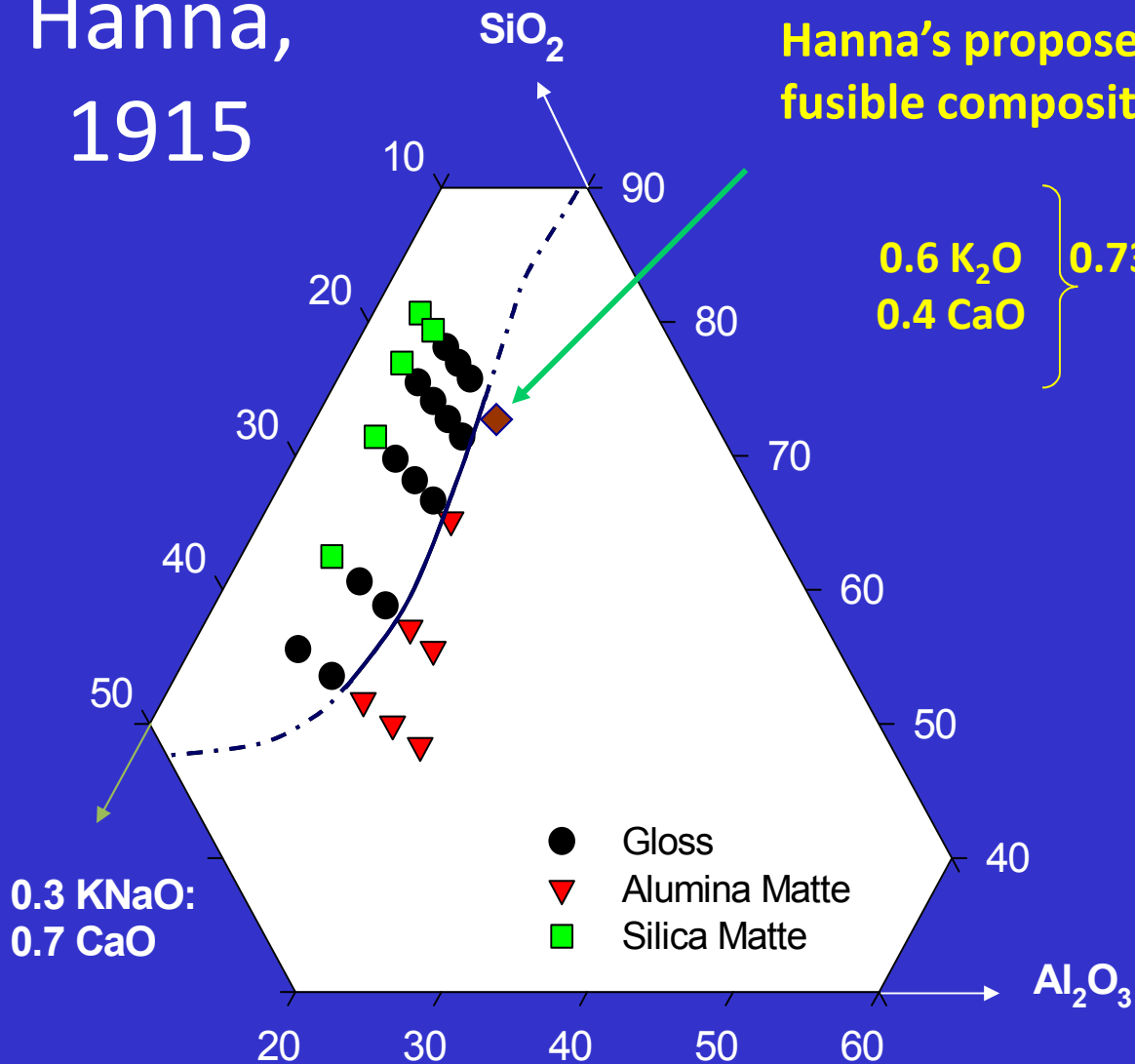
Liquid formation facilitates atomic mobility.

Diffusion of ions within the melt improves the uniformity.

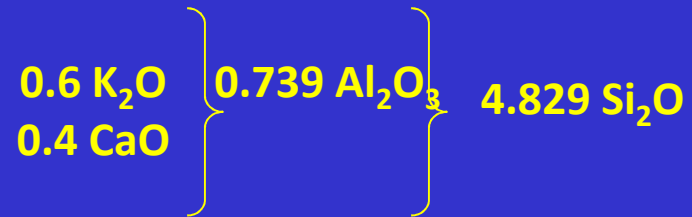
Well melted glazes are chemically uniform (always true for glosses?).

Raw glaze melting starts at a eutectic composition (*proposed – Hanna*).

Hanna,
1915



Hanna's proposed composition of most fusible composition:

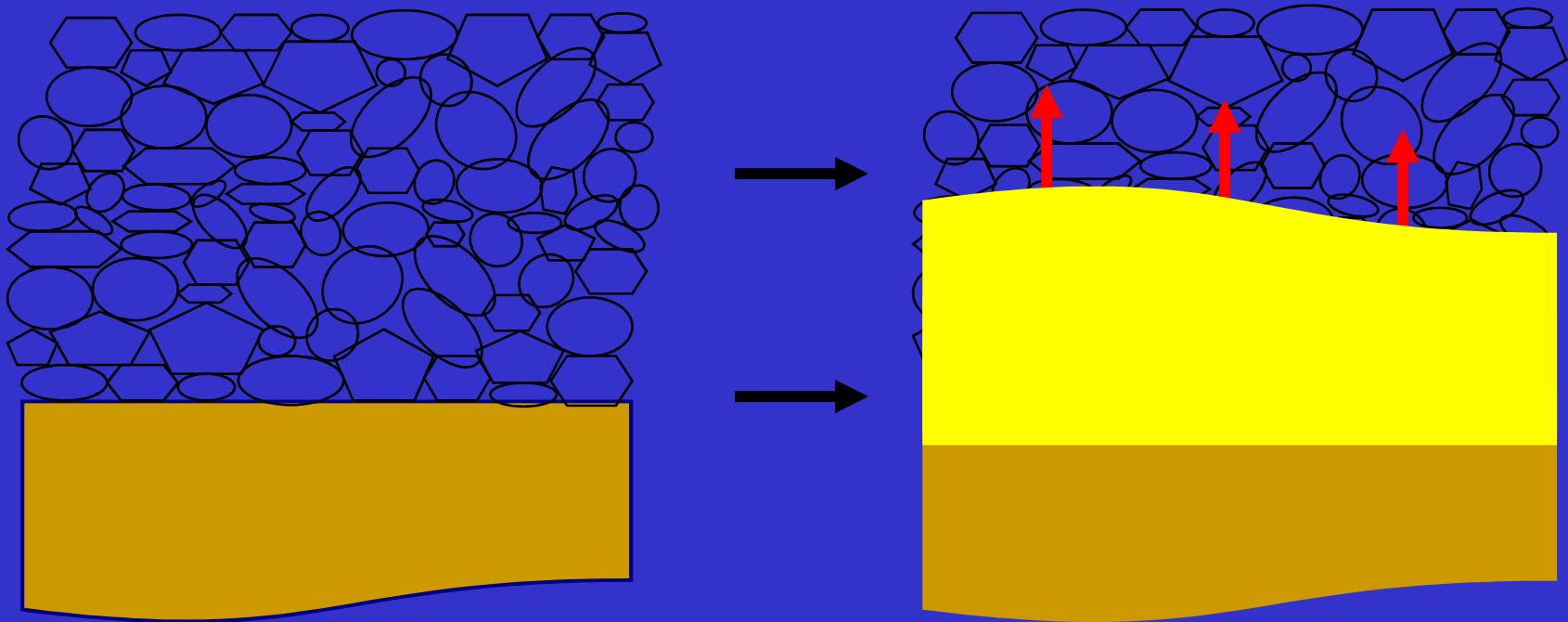


This composition
"fuses" at Cone 3.

Proposal: Raw glazes melt from the body out to the surface

Localized melting in pockets at the glaze-body interface.

Pools of liquid form and particles “melt” into them to eventually form a continuous melt.



Why Does Melt Start at Body?

The body is rich in alumina

The body is rich in silica

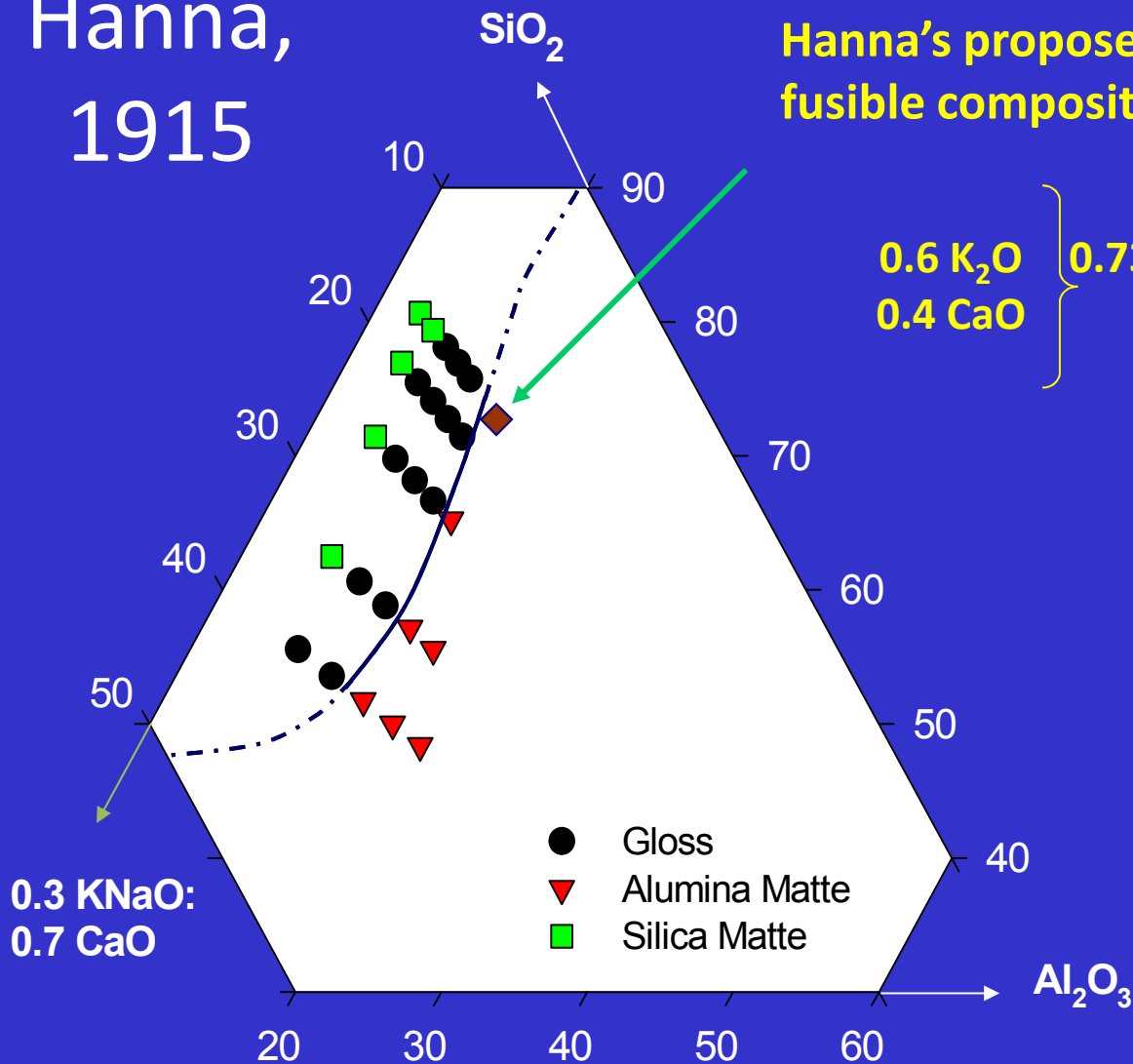
The glaze is rich in RO (CaO, etc.)

The level of R_2O is nearly equivalent between glaze and body (no movement).

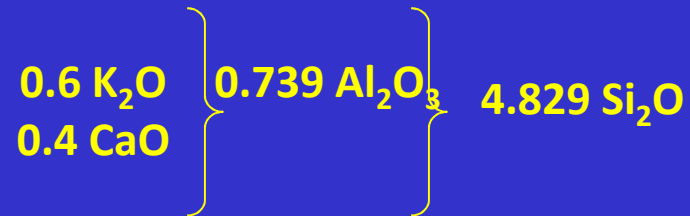
A chemistry exchange at the glaze-body interface results in a eutectic melt: *"Hanna's Eutectic"*

CaO moves into the body; silica and alumina move into the glaze.

Hanna,
1915



Hanna's proposed composition of most fusible composition:



This composition
"fuses" at Cone 3.

Body Glaze Chemistry Exchange

Glaze Example

0.3 K₂O
0.7 CaO

0.35
Al₂O₃

3.5
Si₂O

*Glaze-Body Interface
(Hanna's Eutectic)*

0.6 K₂O
0.4 CaO

0.739
Al₂O₃

4.829
Si₂O

*Typical Body Glass Phase
Chemistry*

1.0 K₂O
0.0 CaO

1.19
Al₂O₃

17.0
Si₂O



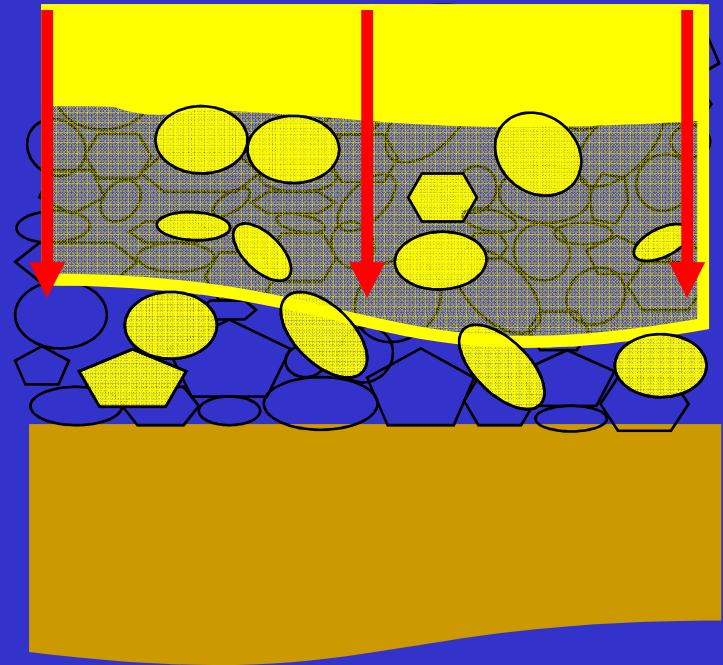
How Frits Melt: *A Proposal*

Frits are powdered glass

Melt similar to ice

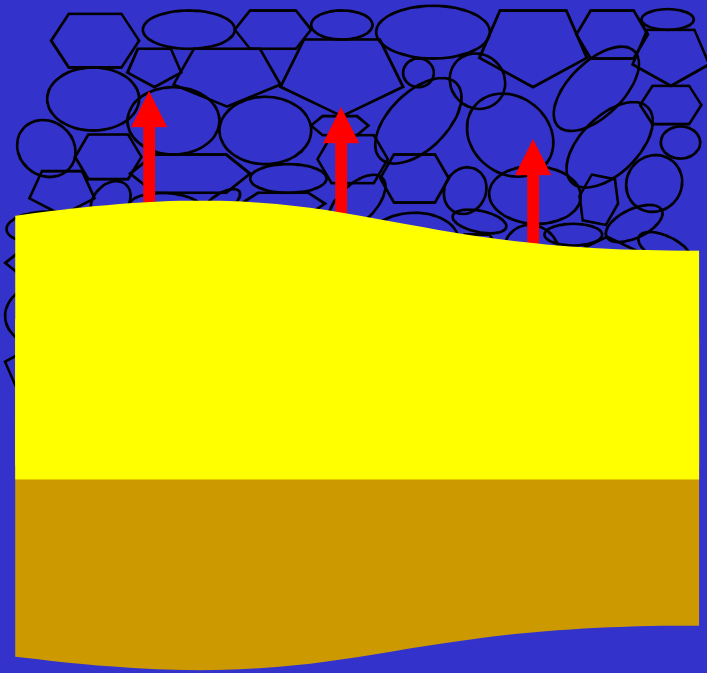
Particles melt uniformly,
or “soften” rapidly
upon reaching melting
temperature

This is “re-melting” as the frit
was previously melted
when it was made (at the
frit factory)

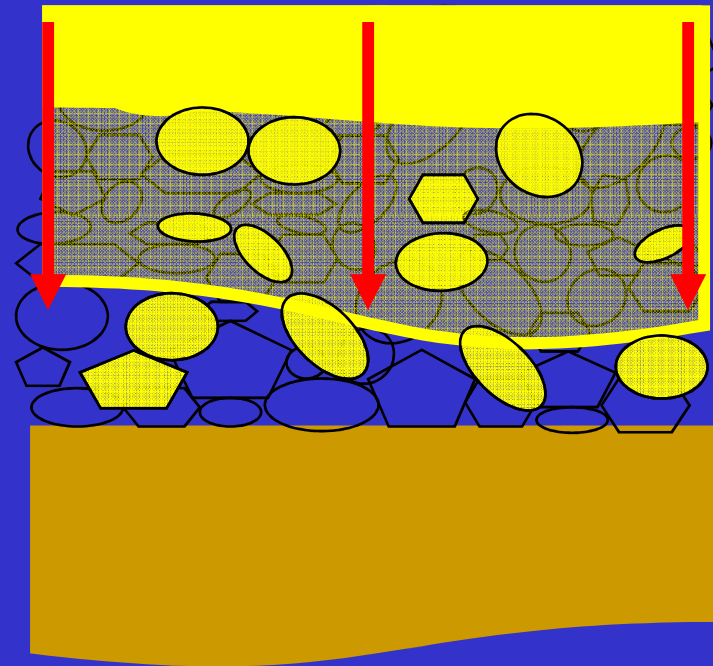


Comparison

Raw Glazes



Glazes with Frit

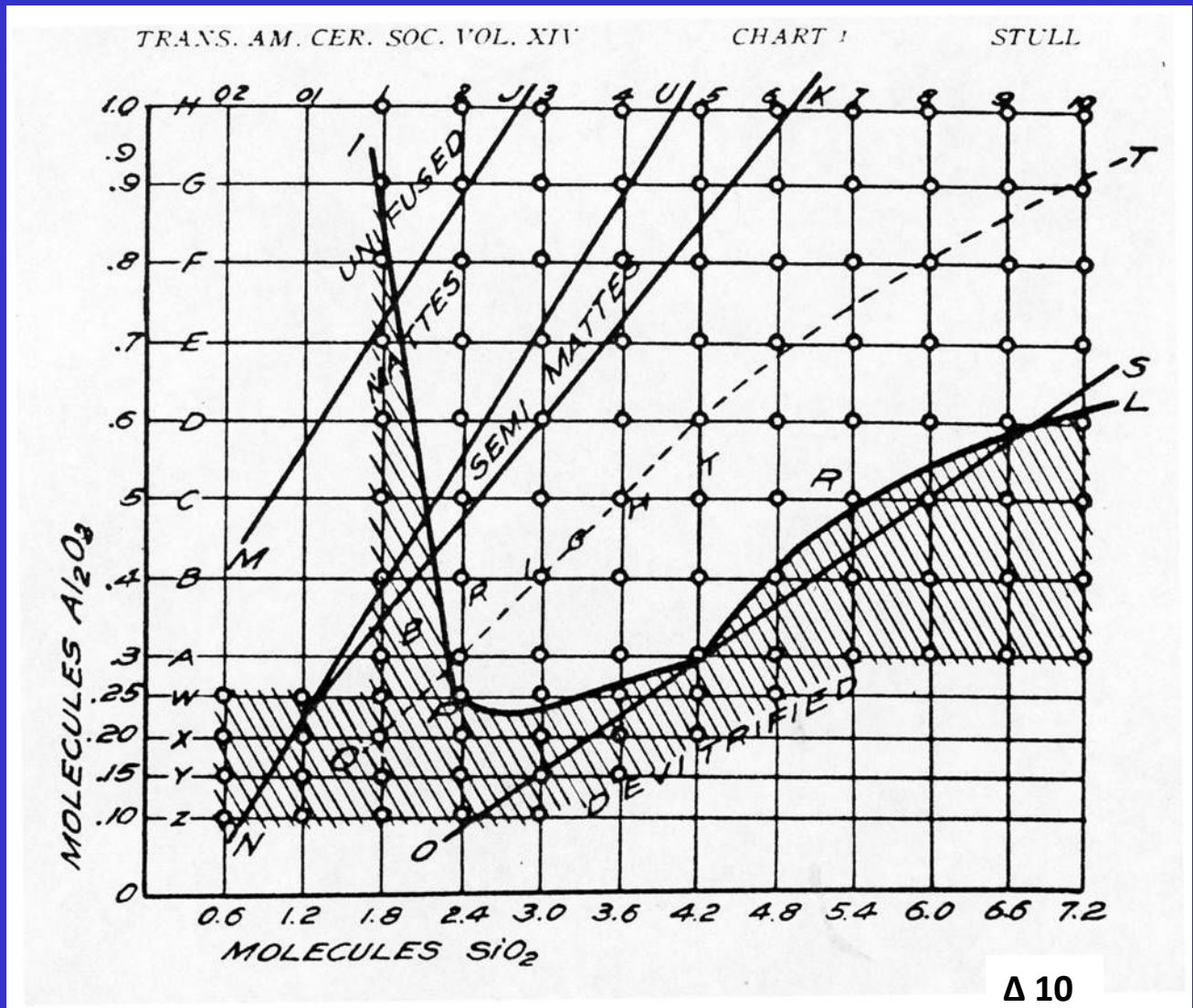


Science!

A map of glaze compositions
& texture

Stull · 1912

0.3:0.7 $R_2O:RO$



Quick background

Silica is a glass former.

Alumina modifies a glass.

Fluxes reduce melting temperature.

The Unity Molecular Formula systematically relates these chemistries to each other.

Useful glaze chemistry shorthand

Shows ratio of glass formers to fluxes

UMF can be used to predict glaze behavior

UMF-Example



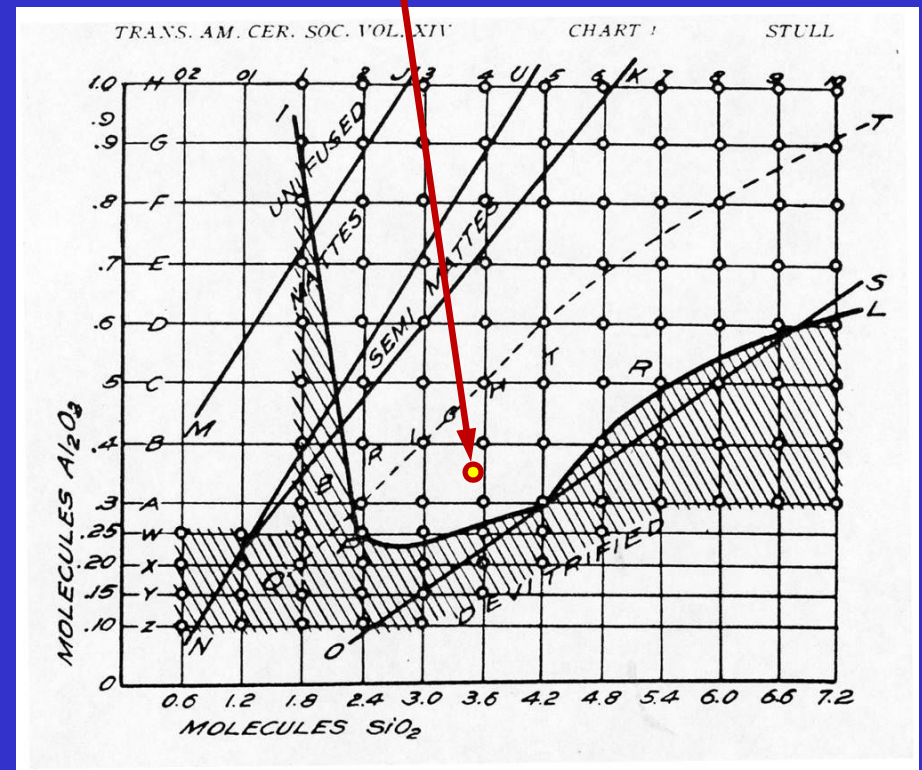
One mole of flux (combined):

0.3 alkali oxides (R_2O)

0.7 alkaline earth oxides (RO)

0.35 moles of alumina (Al_2O_3)

3.5 moles of silica (SiO_2)



UMF Prediction (via Stull)



Melt between cone 5 and cone 10

Won't run off ware

Glossy (Actually, a good single-fire gloss glaze)

Chemically Durable

Mechanically Durable

This chemistry approach was invented by Hermann Seger

Stull's work was based on
that of Seger.

Seger invented Cones
(1895).

Cone 4 was the first cone
Incremental proportions of
silica:alumina for each
mole of flux.

Cone	R ₂ O:RO	Alumina	Silica
1	0.3:0.7	0.1	1
2	0.3:0.7	0.2	2
3	0.3:0.7	0.3	3
4	0.3:0.7	0.4	4
5	0.3:0.7	0.5	5
6	0.3:0.7	0.6	6
7	0.3:0.7	0.7	7
8	0.3:0.7	0.8	8
9	0.3:0.7	0.9	9
10	0.3:0.7	1.0	10
11	0.3:0.7	1.1	11
12	0.3:0.7	1.2	12

Important details

This 0.3 R₂O: 0.7 RO flux ratio is important.

Specifies the ratio of the two different flux families used in glazes.

More in a minute.

The ratio of the fluxes determines the durability of a glaze

More from Matt.

Periodic Table of the Elements

Periodic Table -- Oxide glass forming classification

Alkali metals
+1

Alkaline earth
+2

Glass former*

Intermediate**

Modifier***

Representative elements
+3 +4 +/- 3, 5 -2

Halogens
-1

Noble gases
0

Glass former / Intermediate

Intermediate / Modifier

Transition Metals
+3 +4 +5 +2, 3, 6 +7 +2, 3 +2, 3 +1, 2 +2

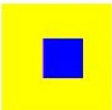
Rare Earths

Lanthanides

Actinides

1.008 1 H Hydrogen																	4.003 2 He Helium						
6.941 3 Li Lithium	9.012 4 Be Beryllium																	10.81 5 B Boron	12.01 6 C Carbon	14.01 7 N Nitrogen	16.00 8 O Oxygen	19.00 9 F Fluorine	20.18 10 Ne Neon
22.99 11 Na Sodium	24.31 12 Mg Magnesium																	26.98 13 Al Aluminum	28.09 14 Si Silicon	30.97 15 P Phosphorus	32.07 16 S Sulfur	35.45 17 Cl Chlorine	39.95 18 Ar Argon
39.10 19 K Potassium	40.08 20 Ca Calcium	44.96 21 Sc Scandium	47.88 22 Ti Titanium	50.94 23 V Vanadium	52.00 24 Cr Chromium	54.94 25 Mn Manganese	55.85 26 Fe Iron	58.93 27 Co Cobalt	58.69 28 Ni Nickel	63.55 29 Cu Copper	65.39 30 Zn Zinc	69.72 31 Ga Gallium	72.61 32 Ge Germanium	74.92 33 As Arsenic	78.96 34 Se Selenium	79.90 35 Br Bromine	83.80 36 Kr Krypton						
85.47 37 Rb Rubidium	87.62 38 Sr Strontium	88.91 39 Y Yttrium	91.22 40 Zr Zirconium	92.91 41 Nb Niobium	95.94 42 Mo Molybdenum	(97.91) 43 Tc Technetium	101.1 44 Ru Ruthenium	102.9 45 Rh Rhodium	106.4 46 Pd Palladium	107.9 47 Ag Silver	112.4 48 Cd Cadmium	114.8 49 In Indium	118.7 50 Sn Tin	121.8 51 Sb Antimony	127.6 52 Te Tellurium	126.9 53 I Iodine	131.3 54 Xe Xenon						
132.9 55 Cs Cesium	137.3 56 Ba Barium	138.9 57 La Lanthanum	178.5 72 Hf Hafnium	180.9 73 Ta Tantalum	183.8 74 W Tungsten	186.2 75 Re Rhenium	190.2 76 Os Osmium	192.2 77 Ir Iridium	195.1 78 Pt Platinum	197.0 79 Au Gold	200.6 80 Hg Mercury	204.4 81 Tl Thallium	207.2 82 Pb Lead	209.0 83 Bi Bismuth	(209) 84 Po Polonium	(210) 85 At Astatine	(222) 86 Rn Radon						
(223.0) 87 Fr Francium	(226) 88 Ra Radium	(227.0) 89 Ac Actinium	(261) 104 Unq Dubnium	(262) 105 Unp Joliotium	(263) 106 Unh Rutherfordium	(262) 107 Uns Bohrium	(265) 108 Uno Hahnium	(266) 109 Une Meitnerium	(272) 110 Uun Ununnilium														
Rare Earths			Lanthanides																				
			140.1 58 Ce Cerium	140.9 59 Pr Praseodymium	144.2 60 Nd Neodymium	(145) 61 Pm Promethium	150.4 62 Sm Samarium	152.0 63 Eu Europium	157.3 64 Gd Gadolinium	159.0 65 Tb Terbium	162.5 66 Dy Dysprosium	164.9 67 Ho Holmium	167.3 68 Er Erbium	169.0 69 Tm Thulium	173.0 70 Yb Ytterbium	175.0 71 Lu Lutetium							
			Actinides																				
			232.0 90 Th Thorium	231.0 91 Pa Protactinium	238.0 92 U Uranium	(237) 93 Np Neptunium	(244) 94 Pu Plutonium	(243) 95 Am Americium	(247) 96 Cm Curium	(247) 97 Bk Berkelium	(251) 98 Cf Californium	(252) 99 Es Einsteinium	(257) 100 Fm Fermium	(258) 101 Md Mendelevium	(259) 102 No Nobelium	(262) 103 Lr Lawrencium							

Alkali Metals (R₂O)

6.941	3
Li	
Lithium	
22.99	11
Na	
Sodium	
39.10	19
K	
Potassium	

These flux families work together.

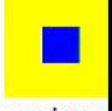



Activates melting.

Gets the melt started.


Too much softens, weakens glaze.

Complimentary flux.
Keeps glazes stable.
Too much melts poorly.

Alkaline Earths (RO)

24.31	12
Mg	
Magnesium	
40.08	20
Ca	
Calcium	
87.62	38
Sr	
Strontium	
137.3	56
Ba	
Barium	

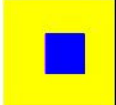
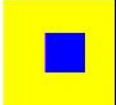
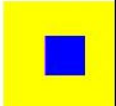
+

65.39	30
Zn	
Zinc	

Why 0.3 R₂O : 0.7 RO flux ratio?
Because it works!

Some General Guidelines for chemistry substitution

Alkali Oxides (R_2O)

6.941	3
Li	
Lithium	
22.99	11
Na	
Sodium	
39.10	19
K	
Potassium	

Alkali can substitute for alkali

Alkaline earth can substitute for
each other.

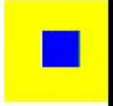

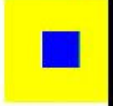

Provided the substitution is on a
molar basis!

Texture is dictated by
silica:alumina ratio

PbO, however,
is a wildcard!

We can also add Fe,
Cu, Co, Ni, and other
RO to this list.

Alkaline Earths (RO)

24.31	12
Mg	
Magnesium	
40.08	20
Ca	
Calcium	
87.62	38
Sr	
Strontium	
137.3	56
Ba	
Barium	

+

65.39	30
Zn	
Zinc	

Historic Chinese Glazes

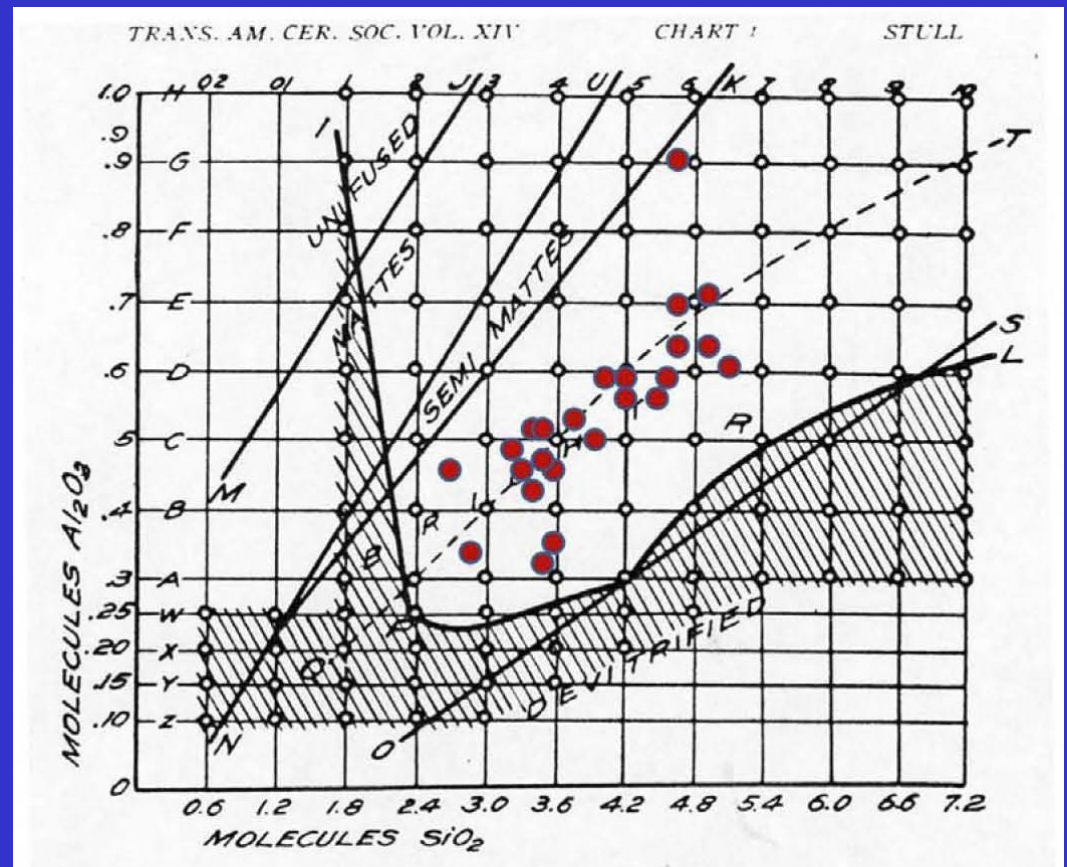
Nigel Wood analyzed ancient Chinese glazes (1999).

UMF format of the analyses is informative.

Most of the glazes fall within glaze limits in use today.

0.3 R_2O : 0.7 RO is the predominant flux ratio.

Glossy glazes fall in Stull's gloss region.



Why? Glaze chemistry determines glaze texture.

Summing Up

Modern Glazes & Ancient Glazes

SIMILAR CHEMISTRY!

It's all about the chemistry!

Now, onto to Mid-range glaze firing and the role of $R_2O:RO$ on durability.