UMF Phase Diagrams: Guidemaps for Ceramic Glaze Development

Written by **Howard Sawhill**

The purpose of this article is to introduce potters to a new type of graph to help them identify composition areas for new glaze recipe development and assist them in producing glazes with desired finishes (e.g. glossy, satin or matt). Potters interested in creating their own ceramic glaze recipes usually start by modifying published glaze recipes. This process can be very systematic through replacement of individual ingredients or simply mixing different glaze recipes together to generate new ones. As endeavor to learn more, they discover the unity molecular formula (UMF) and how it relates to glazes in their firing temperature range of interest as well as some of the limitations of the UMF approach[1].

The next step might be attending an advanced glaze development workshop like one offered by Carty[2], where they are introduced to the ***Stull Diagram*** as a way to demonstrate the impact of glaze chemistry on glaze appearance. Stull[3] published UMF-based diagrams showing how a stoneware glaze surface character changes with different molar amounts of alumina (Al_2O_3) and silica (SiO_2). The Stull Diagram most referenced is based on a stoneware glaze fired at cone 11 with a ratio of 0.7 calcium oxide (CaO)/0.3 potassium oxide (K_2O) fluxes[i]. The UMF-based diagram is a useful means for comparing and contrasting different glazes; good examples are found in the two books by Britt for cone 6[4] and cone 10 glazes[5]. Potters can view their own recipes on a Stull diagram through the ***Glazy*** website (www.glazy.org). Stull diagrams are relevant at cone 6 and possibly lower[6] by addition of Boron to the glaze recipes[7].

Stull's work in 1911 predated much of the advances in ceramic phase diagrams of the 20th century, the first volume published in 1964[8] by the American Ceramics Society. Phase diagrams show how the melting temperature varies with change in composition as well as identifying phases (areas of specific crystal structure) and boundaries between adjacent distinct phases. A more detailed description of phase diagrams can be found at the American Ceramics Society web page[ii]. De Montmollin[9] used phase diagrams to construct and publish a series of 60 fusion (or melting) maps showing the 1300°C (~ Cone 10) boundary within which compositions melt to form glazes at cone 10. He generated UMF diagrams for different ratios of fluxes made up from CaO, MgO and KNaO. Seven years in the making and without the aid of computers, these fusion maps identified areas of glaze melting, thus providing a wide range of fruitful areas for potters to explore.

Taking this approach one step further, transferring key information from published phase diagrams onto a UMF view, a new type of guidemap for glaze development and exploration can be constructed – a ***UMF Phase Diagram***. The UMF Phase Diagram for CaO (Figure 1) was constructed from data points along the phase boundaries and temperature isotherms (the composition along whose lines all melt at the same temperature) in the circled area of the $CaO\text{-}Al_2O_3\text{-}SiO_2$ phase diagram (Figure 2).

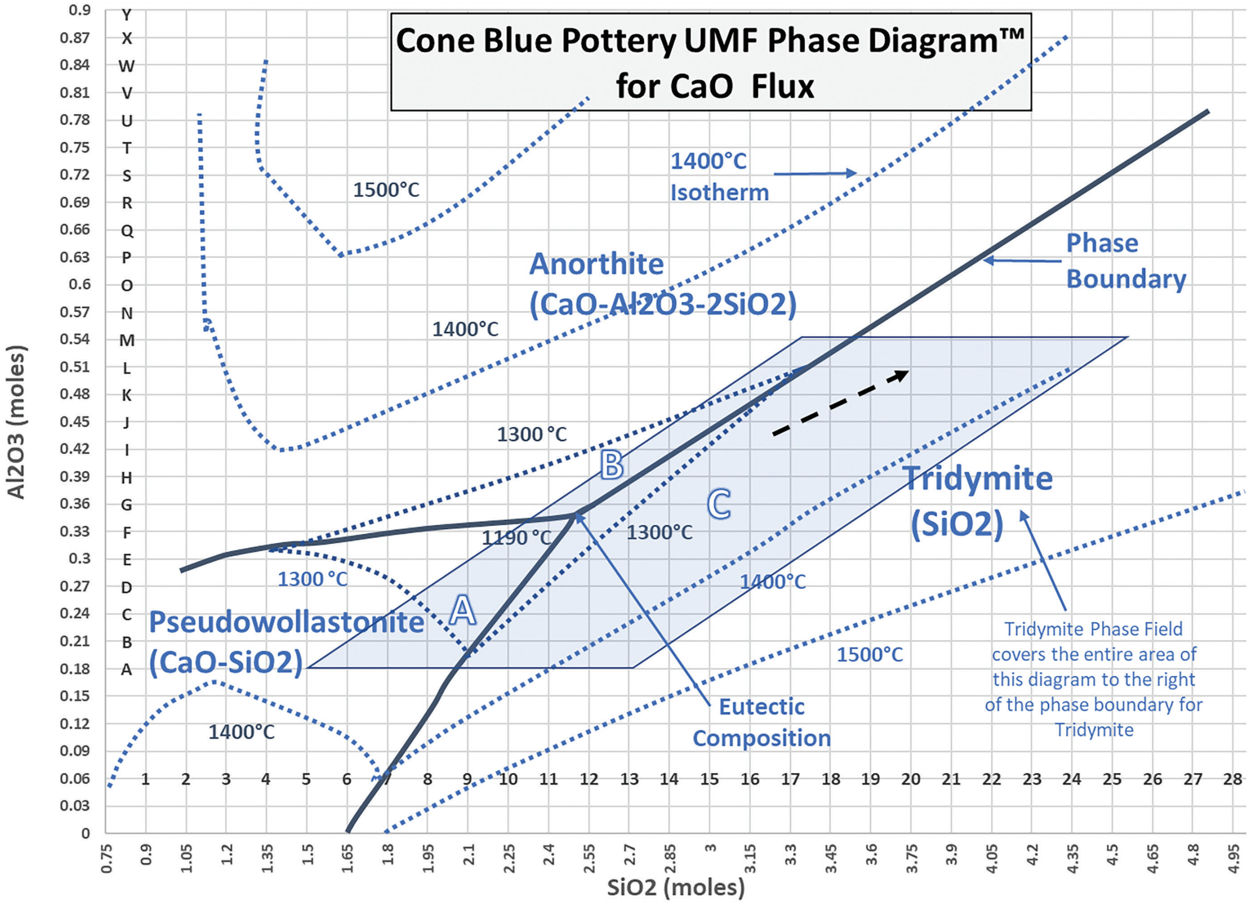
Opposite top: Figure 1. Cone Blue Pottery UMF Phase Diagram™ for CaO: Each location marks a composition with 1 mole of CaO and the moles of Al2O3 and SiO2 indicated in the diagram. The dashed arrow is explained in the paragraph describing Fig 5.

Opposite bottom: Figure 2. Phase Diagram of CaO-Al2O3-SiO2 adapted from reference 10.

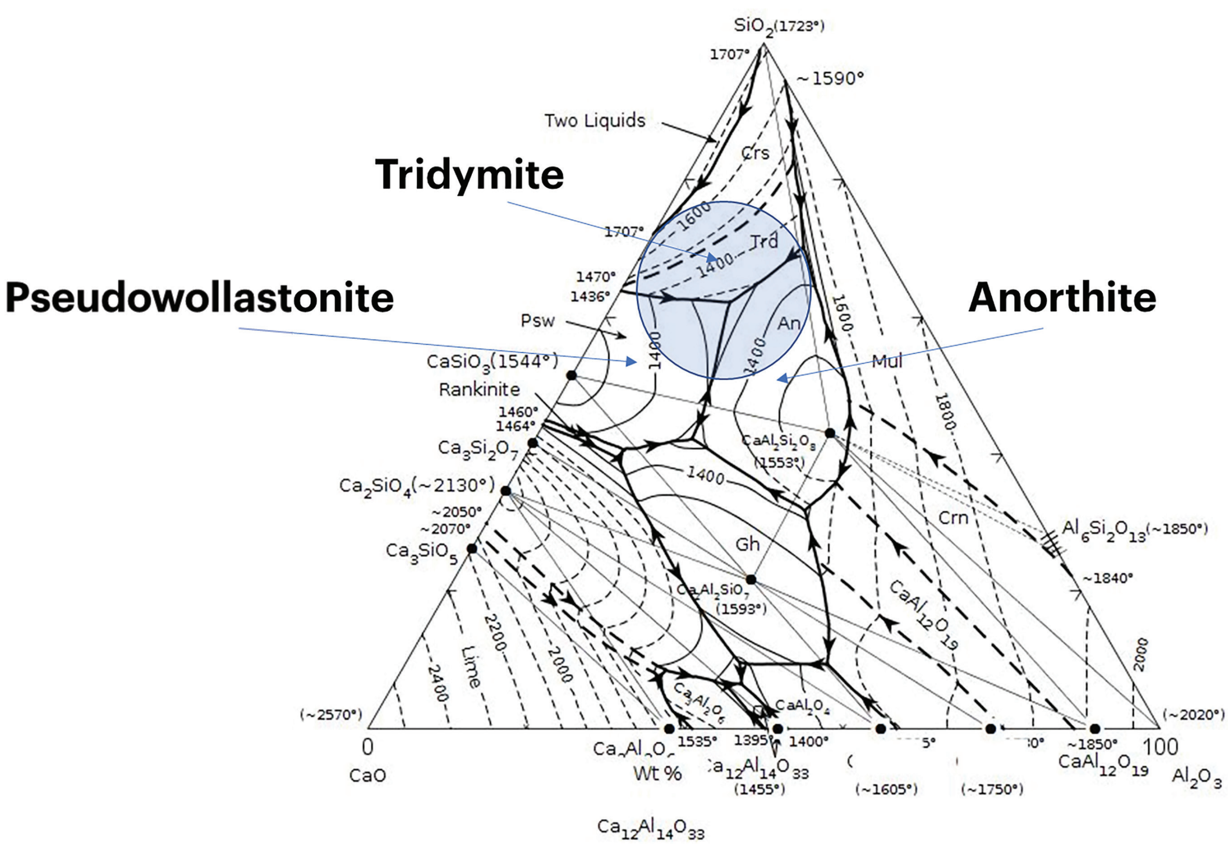
Notes

i. Glaze recipes developed to mimic early Chinese celadon glazes often utilize a similar flux ratio of roughly 0.7 alkaline earth (CaO, MgO) to 0.3 alkali (Na2O, K2O).

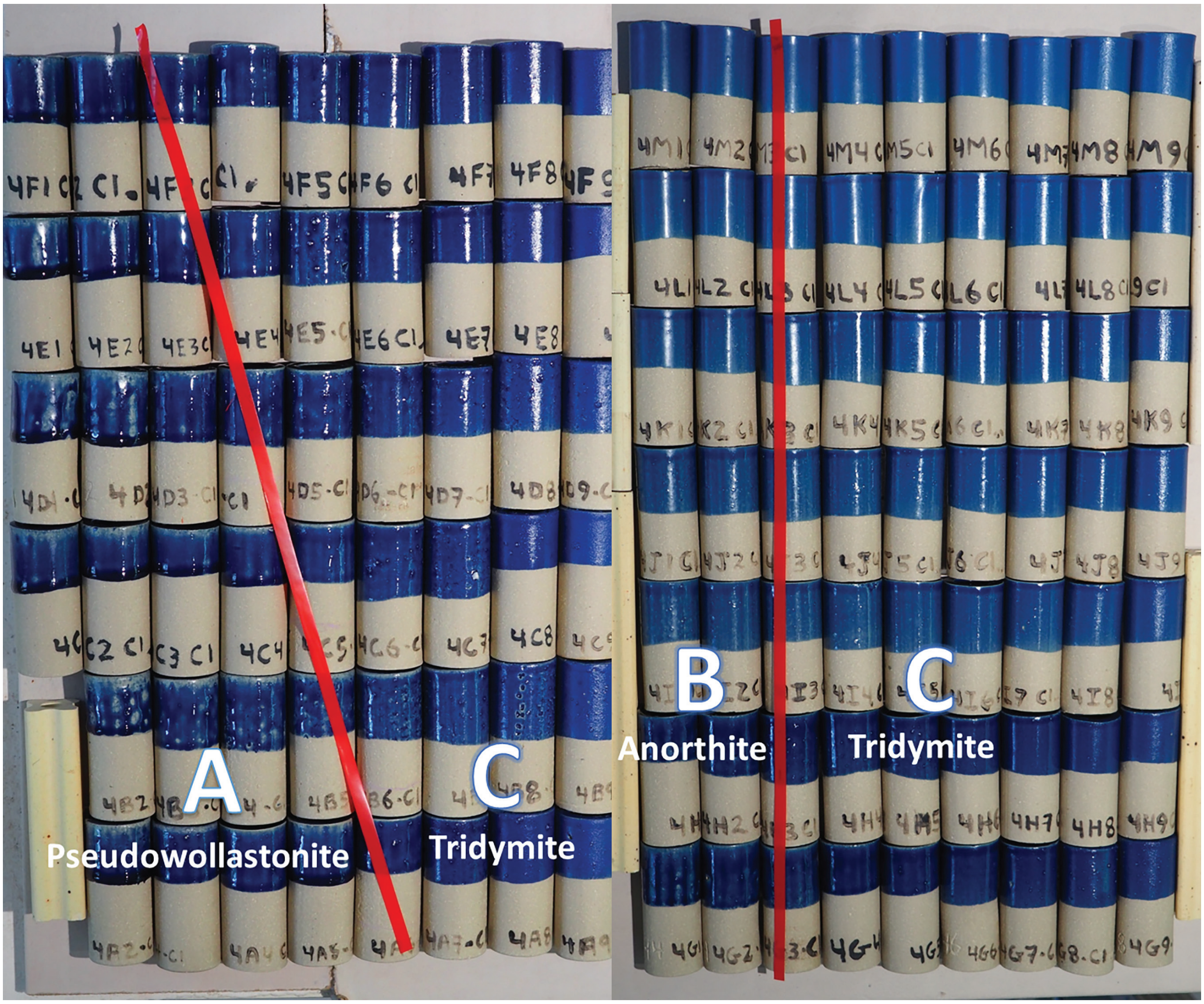
ii. The American Ceramics Society provides online access to over 28K phase diagrams for a license fee (www.ceramics.org) along with selected diagrams in a free demo.

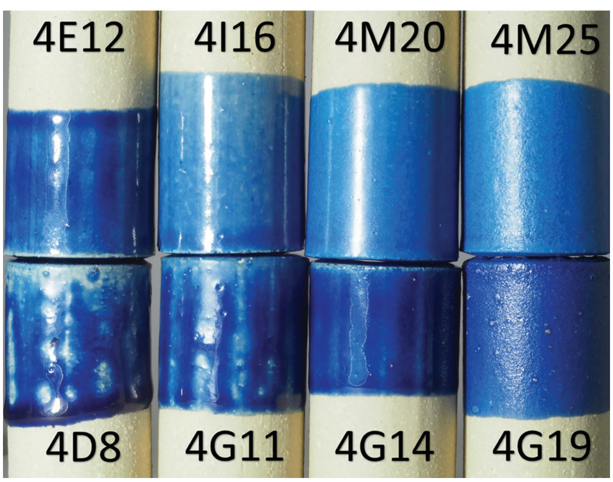


Cone Blue Pottery UMF Phase Diagram™
for CaO Flux
1500°C
1400°C
Isotherm
Anorthite
(CaO-Al2O3-2SiO2)
Phase
Boundary
1400°C
1300 °C
B
C
Tridymite
(SiO2)
1190 °C
1300°C
1300 °C
A
1400°C
Pseudowollastonite
(CaO-SiO2)
1500°C
Tridymite Phase Field covers the entire area of this diagram to the right of the phase boundary for Tridymite
1400°C
Eutectic
Composition
Al2O3 (moles)
SiO2 (moles)



Tridymite
Pseudowollastonite
Anorthite
Two Liquids
Crs
Trd
An
Psw
Mul
Gh
Crn
Lime
CaO
Al2O3
Wt %





Top:
Figure 3. Test tile results from the shaded area in Figure 1.

Above left:
Figure 4. Close up view of selected glaze test tiles. The reflections give hint to the surface smoothness. Test tile codes correspond to compositions shown in Figure 1.

Above right:
Figure 5. Mason stain additions to glossy transparent base glaze 4I16 shown on 3 different clay bodies. Mason stain 6450 Praseodymium maintains the glossy glaze appearance of the base glaze; 6310 Wedgewood Blue becomes satin to matt.

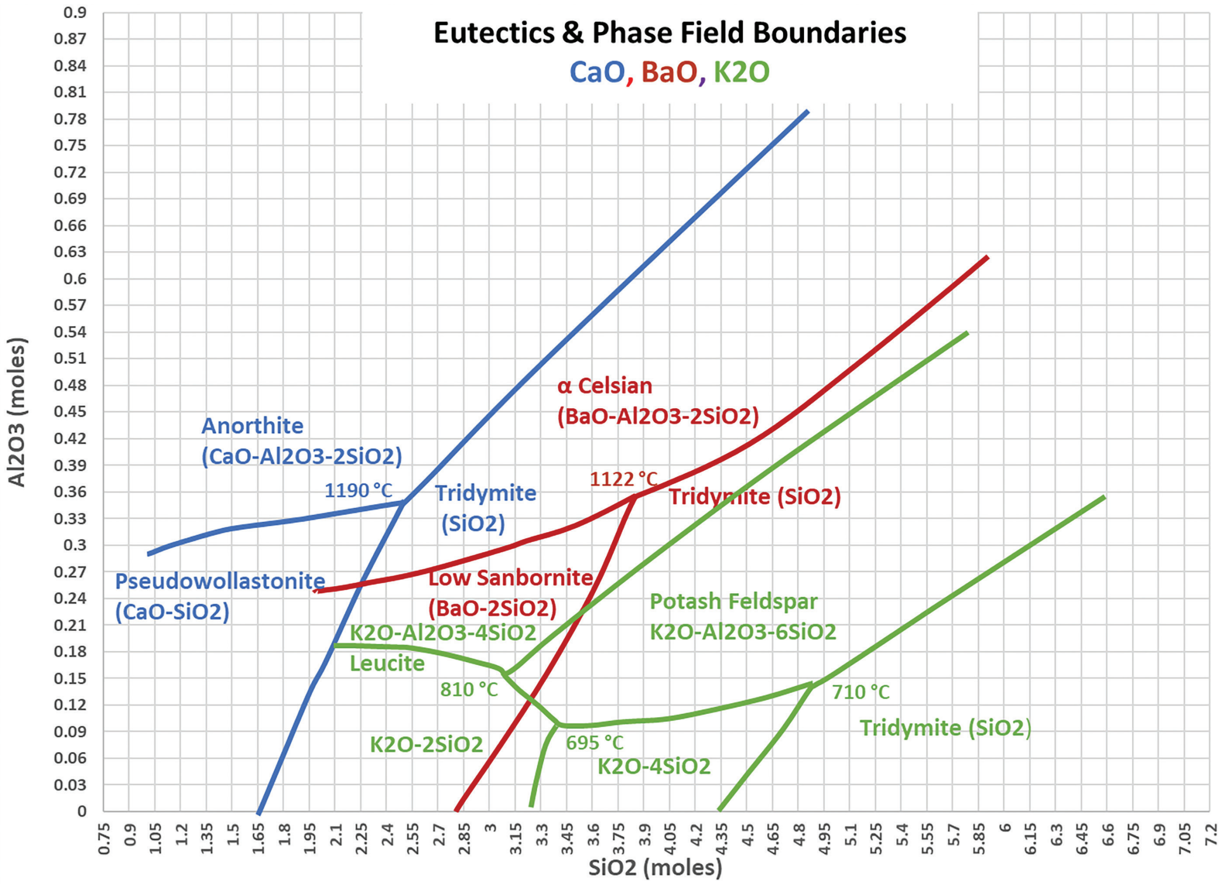
The solid lines in Figure 1 represent the boundaries between the phases, the phase fields are identified by their specific names (viz Tridymite, Anorthite and Pseudowollastonite), and the temperature isotherms are shown using dotted lines. Each point in Figure 1 represents a specific composition containing a molar ratio of 1 mole of CaO (hence the term Unity in UMF) to moles of Al_2O_3 (shown on the vertical axis) and moles of SiO_2 (shown on the horizontal axis). Test tiles are coded with the first number representing the series (4 for CaO, 8 for barium oxide-BaO), the next letter and the following number representing the moles of Al_2O_3 and SiO_2 respectively (see Figure 1). The composition in Figure 1 marked 4I16 thus contains 1 mole of CaO, 0.42 moles of Al_2O_3 and 3.15 moles of SiO_2. To demonstrate some of the utility of this approach, a series of cylindrical test tiles were dipped in glaze and fired to cone 10 in an oxidation kiln. The glazes were made using mixtures of whiting (calcium carbonate that converts to calcium oxide (CaO) on firing), EPK China Clay (EPK) and silica with 0.5% cobalt oxide colorant added to make comparisons easier. For consistency, each glaze consists of 62%solids/38% water with Darvan 7 deflocculant added at 1% of the EPK China Clay weight.

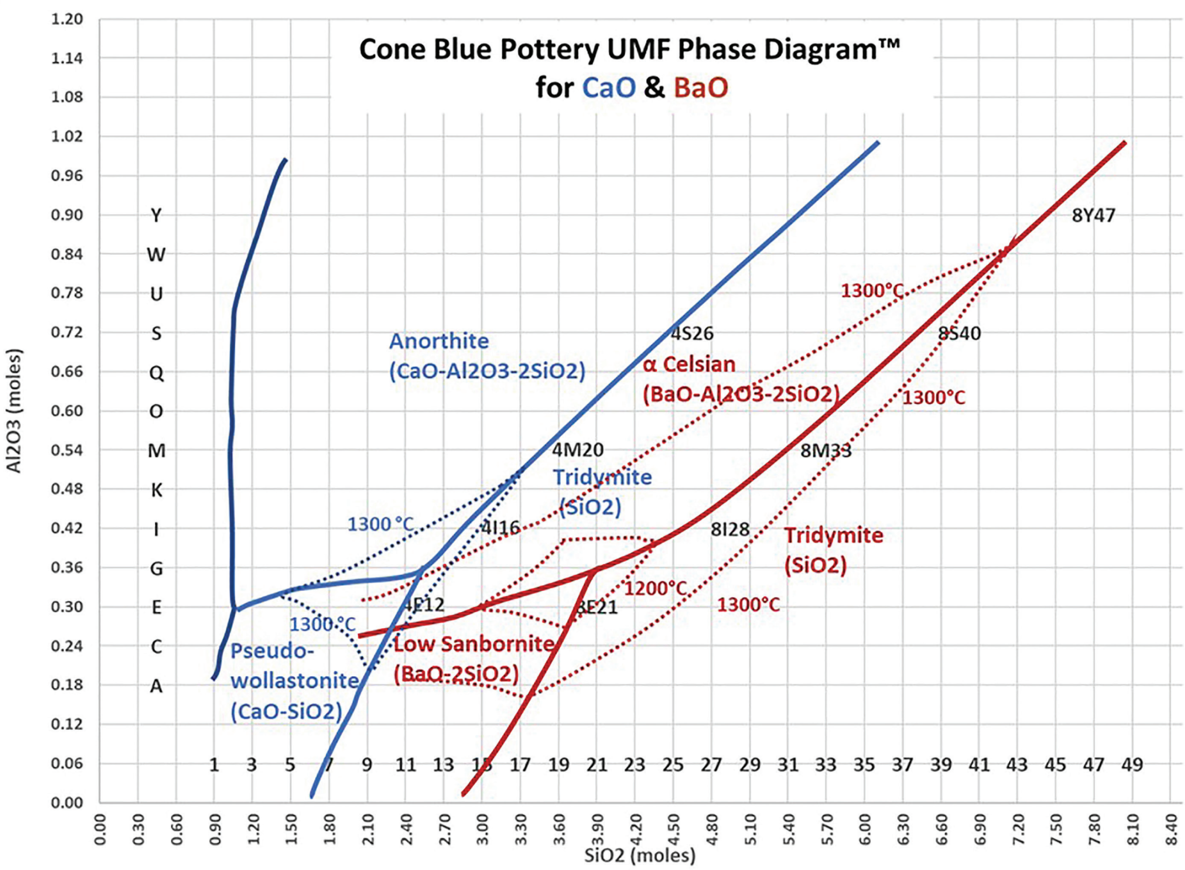
Fired test tiles (Figure 3) from the shaded area of Figure 1 show distinct differences between the three phase areas. Figure 4 shows higher magnification photos of selected tiles from Figure 3. Glazes in area A (Figure 3), the psuedowollastonite phase field, display a glaze finish described as rivulets[11]. Lower melting temperatures near the eutectic created a bottom pooling ring (4D8 in Figure 4). In area B, the anorthite phase field, the glazes no longer pool as in area A; they show a glossy appearance but continue to show rivulets (4G11 in Figure 4). In area C, the tridymite phase field, the glazes show no pooling or rivulets and transition from glossy glazes to rough dry surfaced glazes with increased SiO_2 content (4G14 and 4G19 respectively. With increased EPK content (and a corresponding decrease in CaO flux) glazes just inside the tridymite field progress from bright gloss (4E12) to soft gloss (4I16) to satin (4M20). Satin turns to flat matt, then to textured matt (4M25) with continued increase of SiO_2. Overall, the results indicate a wide range of surface appearance of CaO glazes in the areas studied.

Colorants added to a base glaze (4I16 without the CoO) can change the overall surface appearance, as shown in Figure 5, where 5% of 2 different colorants were added and tested on 3 different clay bodies. Mason stain 6450 Praseodymium maintains the glossy glaze appearance of the base glaze, while 6310 Wedgewood Blue turns the glaze matt. By comparing this matt surface to the test tiles in Figure 3, it's possible to get an estimate of the effective change (indicated by the dashed arrow in Figure 1) imparted by this particular colorant. This provides a strategy, if so desired, to adjust this matt glaze with 6310 back to its original glossy surface by reducing the SiO_2 and Al_2O_3 content following the reverse direction of the dashed arrow.

Figure 6 shows the phase boundaries of BaO, K_2O and CaO. The BaO phase boundaries appear similar to CaO, with a slightly lower eutectic temperature at higher SiO_2 level. The eutectic temperature is where the 3 phase boundaries meet and represents the lowest melting temperature in the region shown. By contrast, K_2O exhibits a more complex series of phase boundaries. Figure 7 compares the CaO and BaO phase boundaries and the temperature isotherms. Just to the inside of the Tridymite phase field of CaO (Figure 7 points 4I16,4M20,4S26) glazes progress from glossy to textured matt based largely on increased EPK content with reduced CaO flux. Table 1 shows the recipes and UMF values for these CaO compositions as well as BaO compositions. Based on the similarity of the phase relationships between CaO and BaO, we could postulate a similar trend in the BaO system (Figure 7 points 8M33,8S40,8Y47). Figure 8 shows this to be the case, revealing similar surfaces for CaO and BaO tiles with comparable relationships to the eutectic point and apex of the 1300°C isotherms. The composition and UMF values of the glazes in Figure 8 are shown in Table 1.

Similar results were obtained from BaO glazes near the left and right 1300°C isotherms. Blends (75/25, 50/50, 25/75) between lower and higher SiO_2 level BaO pairs containing equal Al_2O_3 levels (8E12/8E21, 8I16/8I28 and 8M20/8M33) showed similar glossy appearance. Mixtures (50/50 by weight) of CaO and BaO compositions at equal Al_2O_3 levels show a similar but subtler trend from glossy semi-transparent to glossy opaque with increased EPK content (Figure 9). The introduction of UMF diagrams for CaO and BaO in this article provides a new tool for potters to consider in their approach to developing new glazes with their desired look and feel. ■


Eutectics & Phase Field Boundaries
CaO, BaO, K2O
Al2O3 (moles)
SiO2 (moles)
Anorthite
(CaO-Al2O3-2SiO2)
1190 °C
Tridymite
(SiO2)
α Celsian
(BaO-Al2O3-2SiO2)
1122 °C
Tridymite (SiO2)
Pseudowollastonite
(CaO-SiO2)
Low Sanbornite
(BaO-2SiO2)
Potash Feldspar
K2O-Al2O3-6SiO2
K2O-Al2O3-4SiO2
Leucite
810 °C
710 °C
Tridymite (SiO2)
K2O-2SiO2
695 °C
K2O-4SiO2


Cone Blue Pottery UMF Phase Diagram™
for CaO & BaO
Al2O3 (moles)
SiO2 (moles)
Y
W
U
S
Q
O
M
K
I
G
E
C
A
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35 37 39 41 43 45 47 49
8Y47
1300°C
4S26
8S40
Anorthite
(CaO-Al2O3-2SiO2)
α Celsian
(BaO-Al2O3-2SiO2)
1300°C
4M20
8M33
Tridymite
(SiO2)
1300 °C
4I16
8I28
Tridymite
(SiO2)
1200°C
1300°C
4E12
8E21
1300 °C
Pseudo-
wollastonite
(CaO-SiO2)
Low Sanbornite
(BaO-2SiO2)

Glaze Code	4I16	4M20	4S26	8M33	8S40	8Y47
Whiting (wt.%)	28.86	24.89	22.08			
Barium Carbonate (wt.%)				31.64	27.98	24.32
EPK China Clay (wt. %)	32.65	36.27	38.17	23.29	26.82	30.35
Silica (wt.%)	38.49	38.84	39.75	45.07	45.2	45.33
Cobalt Oxide (wt.%)	0.5	0.5	0.5	0.5	0.5	0.5
UMF Flux-Al2O3-SiO2	1-0.42-3.15	1-0.54-3.75	1-0.72-4.65	1-0.54-5.7	1-0.72-6.75	1-0.9-7.8

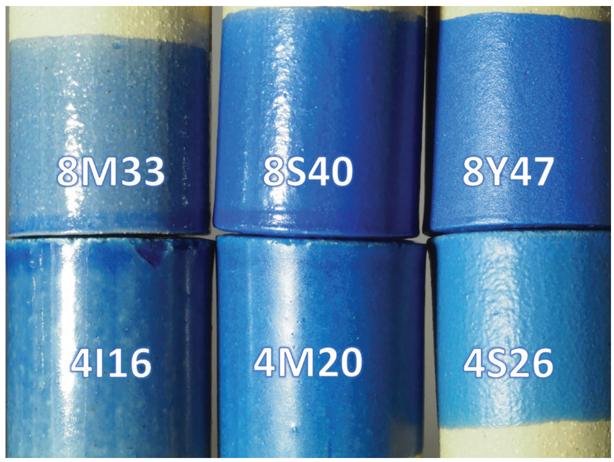
Table 1: Recipes and UMF values for test tiles shown in Fig 8.

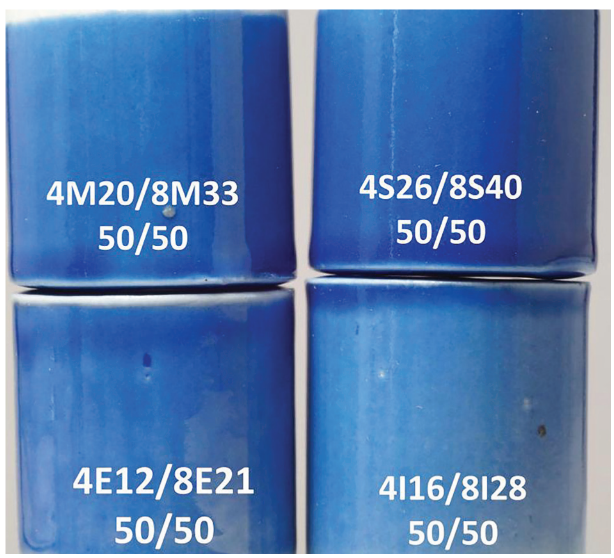
Opposite top: *Figure 6.* Phase fields, phase boundaries and eutectics for CaO, BaO and K2O fluxed glazes.

Opposite bottom: *Figure 7.* Cone Blue Pottery UMF Phase Diagram™ of both BaO and CaO.

Right top: *Figure 8.* Test tiles from compositions just inside the Tridymite phase field of CaO (series 4) and BaO (series 8) with increasing EPK and decreasing flux content. Test tile codes correspond to compositions shown in Figure 7.

Right bottom: *Figure 9.* Mixtures of CaO fluxed and BaO fluxed glazes with increasing EPK and decreasing flux content. Test tile codes correspond to compositions shown in Fig 7.





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Further Information

Examples of glaze research and development studies, collaborations, videos and contact information can be found on the website www.conebluepottery.com.

About the Author

Howard Sawhill's introduction to ceramics came in junior high school, when braces kept him from playing trumpet in band, thus landing him in art class where he sat across the table from the school's two best artists. When the class shifted medium – from drawing to working with clay – he knew ceramics was in his future. After graduating from MIT with a Ph.D. in Ceramics, he worked 30 years with DuPont Electronics, leading research and development teams that introduced new ceramic-based products into the marketplace. In his second career he started Cone Blue Pottery, where the mainstay is research and development of ceramic glazes. He is currently working in collaboration with potters on challenging glaze issues, and performing glaze studies aimed at the improved understanding of glaze performance.