# Investigation on the Effects of Drying Time and Age of Glaze on a Macrocrystalline Glaze & An Analysis on Spherulite Growth

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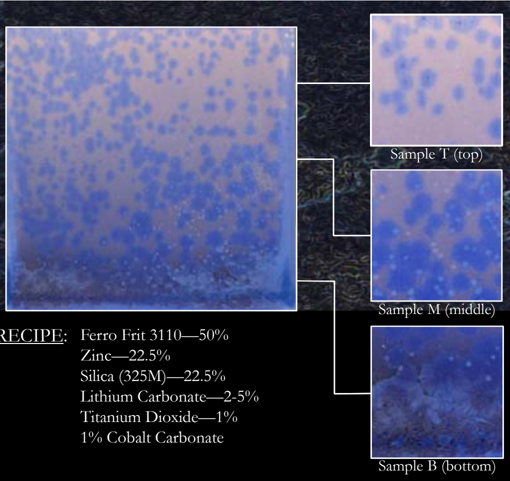
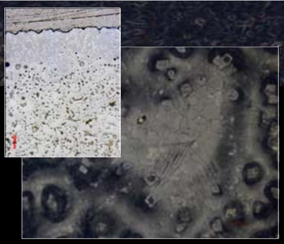


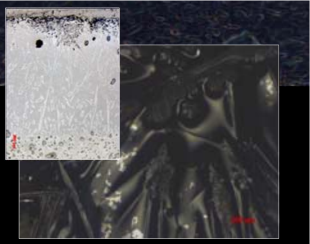
RECIPE:
- Ferro Frit 3110—50%
- Zinc—22.5%
- Silica (325M)—22.5%
- Lithium Carbonate—2-5%
- Titanium Dioxide—1%
- 1% Cobalt Carbonate

Each sample was glazed and fired with the same firing schedule. All samples appeared as above with no visible affect from age of glaze or drying time. However, there was a progression of spherulite growth. The thicker glaze at the bottom run-off had larger spherulites, which were more defined, bluer, and more glassy.

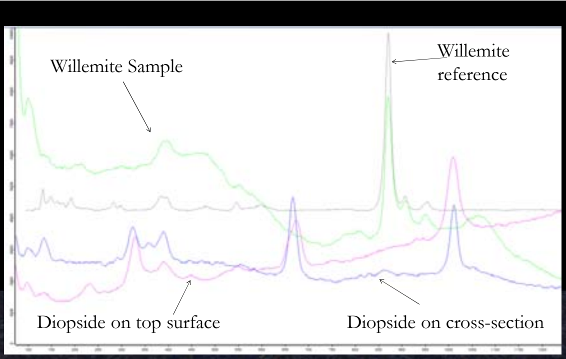
**INTRODUCTION**--The production of spherulites in a macrocrystalline glaze is complicated and difficult to consistently reproduce. Specific compositions and conditions are required for success. Two conditions – drying time and the age of the glaze batch – are explored here to determine their effect on the macrocrystalline glaze behavior. Glaze from a single batch was applied on ceramic tiles on separate days and dried for different durations. All samples were fired with the same firing schedule. Analysis revealed that drying time and age of the glaze had little effect on the production of spherulites. However, there were differences in spherulite size, definition, color, and clarity of the glaze within single samples which appear to be dependent on glaze thickness.


Sample T, cross-section, glaze thickness is ~100 µm (left), surface (right).

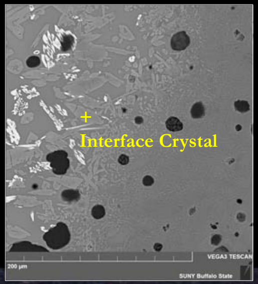

Sample M, cross-section, glaze thickness is ~200 µm (left), surface (right).


Sample B, cross-section, glaze thickness is ~1400 µm (left), surface (right).

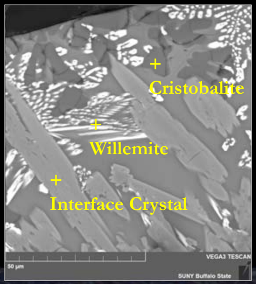
OPTICAL MICROSCOPY--(*left to right*, Sample T, M, and B) Samples T and M have cubic crystals causing a matte surface. In comparison to T and M, B has matured spherulites with a developed nucleus and longer, larger, and more distinct radial acicular needles. Needles were identified by Raman as willemite, which is expected from macrocryaline spherultes.



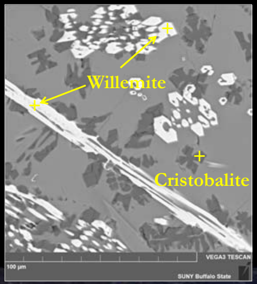
RAMAN SPECTROSCOPY (x-axis is wavenumbers (cm$^{-1}$) and y-axis is intensity) -- Acicular needles were confirmed to be willemite (Zn$_2$SiO$_4$). Cubic surface crystals located on the surface of Sample T and M were identified as diopside (MgCaSi$_2$O$_6$)O$_6$.



Sample B, backscattering SEM image of glaze-body interface.



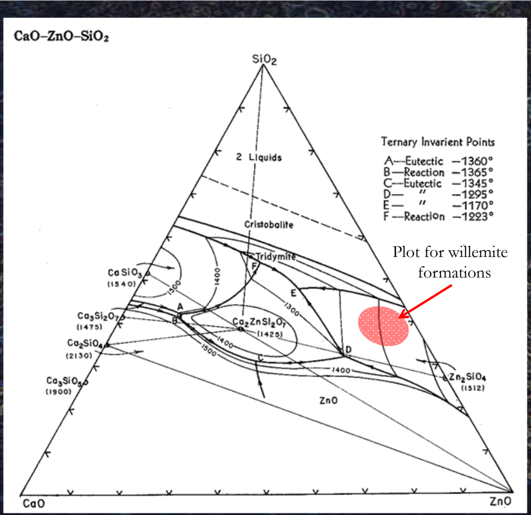
Sample T, backscattering SEM image of glaze cross-section.



Sample B, backscattering SEM image of glaze cross-section.

SEM — Porosity at the glaze-ceramic interface and crystal growth from the ceramic body indicate interface vitrification and that the glaze and body were compatible materials.

SEM-EDS identified elemental compositions corresponding to willemite, cristobalite, and crystals growing from the ceramic body at the interface with the glaze. The glaze thickness after run-off ranged from 100 µm (T) to 1,400 µm (B). The thicker the glaze, the more cristobalite, and the less the interface crystals impede willemite formation that occurs near the glaze surface.



Elemental analysis corresponding to willemite (Zn$_2$SiO$_4$) fell into the willemite formation region on the CaO-ZnO-SiO$_2$ ternary phase diagram.

Elemental analysis corresponding to cristobalite fell into the cristobalite formation region on the CaO-MgO-SiO$_2$ ternary phase diagram.

The phase diagram indicates that an increase in SiO$_2$ can cause a crystalline phase change from diopside (responsible for matte appearance) to cristobalite. Thicker glaze led to an increase in cristobalite formation and decrease in diopside formation.

CONCLUSION – Visual examination and instrumental analysis indicated that drying time and the age of the glaze do not play a major role in willemite spherulite production. However, each sample showed that spherulite maturity and clarity of the glaze were affected by the thickness of glaze. A matte glaze was attributed to the recalcination of diopside. It appears that diopside interferes with willemite formation in thin glazes, but may be avoided at higher firing temperatures or thicker glaze application. The sample with the thickest glaze had longer three-dimensional acicular needles, more glaze area for the willemite crystals to grow without interference, a more silica-rich glaze (cristobalite), and glass-like glaze with no diopside formation.

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