TECHNO FILE

phase and eutectics

by Linda Bloomfield

Making glazes and adjusting their formulation to change their properties is a subject that many potters find daunting. Knowing how your materials interact in a glaze may help you through the process.

Defining the Terms

Eutectic: The lowest melting temperature combination of two or more materials.

Liquidus Line: The line in a phase diagram above which only liquid is present.

Melting Point: The temperature at which a solid will melt.

Phase: Gas, liquid, solid, or solid with a particular crystal structure.

Phase Diagram: A chart of composition against temperature, showing the different phases: solid and liquid.

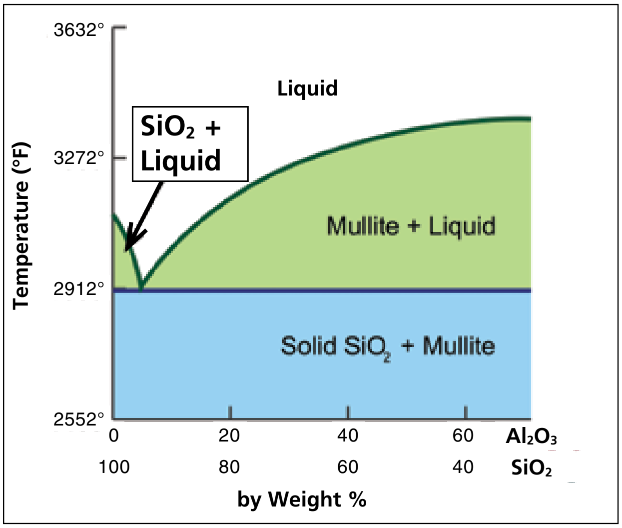
Phase Changes

There are three phases of matter: solid, liquid, and gas. Many substances that are solid at room temperature can be heated up until they melt to become a liquid, and then heated still further until they vaporize and become a gas (ice becomes water, which vaporizes to steam). However, when two materials are mixed together, the melting point of the mixture is often lower than that of either of the pure materials (for example, milk chocolate melts at a lower temperature than plain dark chocolate). This happens when silica and alumina are mixed in glazes. The melting point of silica is 3110°F (1710°C) and that of alumina is 3722°F (2050°C). At the eutectic point, when 10% alumina and 90% silica are mixed, the melting point is only 2813°F (1545°C). All other ratios of silica and alumina have higher melting points.

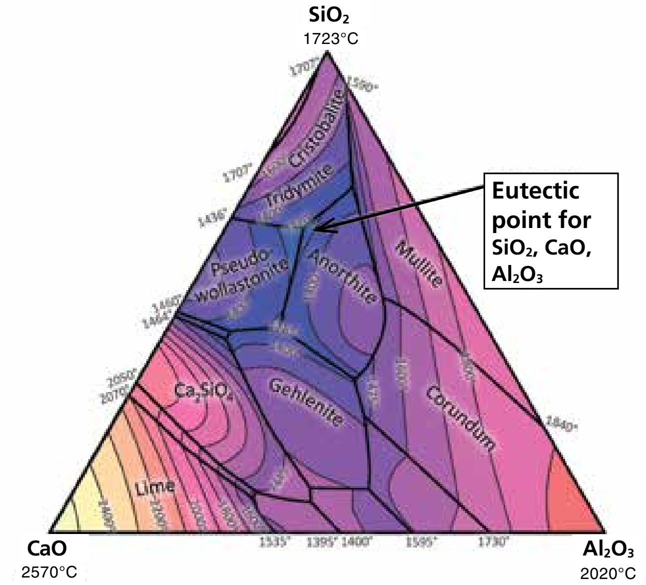
A phase diagram shows the different phases, primarily solid and liquid, and how they change with temperature. In the binary phase diagram for silica and alumina (1), the liquid mixture is at the top, the solid mixture at the bottom, and below the green "liquidus" line, solid silica plus liquid on the left and solid mullite ($3Al_2O_3{\cdot}2SiO_2$) plus liquid on the right. In these areas, melting takes place slowly, over a range of temperatures. However, at the eutectic point (the lowest-melting combination), complete melting occurs at a specific temperature. Mullite (named after the Isle of Mull in Scotland) grows in needle-shaped crystals during firing, and helps to vitrify the clay body and make the glaze-body interface, which gives strength to the fired pottery. Mullite forms only in or near the surface of the clay, where there is excess alumina available.

Fluxes

The melting temperature can be lowered further by adding a flux, which forms a eutectic with the silica. The fluxes each form their own eutectic with silica and alumina, lowering the melting point. For example, 23.25% calcia, 14.75% alumina, and 62% silica melts at 2138°F (1170°C). In practice,



1 Simplified phase diagram for silica-alumina. The eutectic point is the lowest-melting combination of silica and alumina. Mullite is a compound of alumina and silica $3Al_2O_3{\cdot}2SiO_2$. Each phase is separated by a line: liquid, solid (blue) and mixtures of liquid with solid crystals (green).



2 Phase diagram for silica-alumina-calcia. The contour lines show temperature (blue is relatively cool, red and yellow are hot). The eutectic point is the lowest-melting combination at 2138°F (1170°C). Lime is calcium oxide; wollastonite is calcium silicate, corundum is alumina, mullite is alumina-silicate, cristobalite and tridymite are silica phases and anorthite is calcium feldspar.

Alkali	Formula	Temperature °F	Temperature °C
Potassia	$K_2O\cdot Al_2O_3\cdot SiO_2$	1283°	695°
Soda	$Na_2O\cdot Al_2O_3\cdot SiO_2$	1350°	732°
Lithia	$Li_2O\cdot Al_2O_3\cdot SiO_2$	1787°	975°
Alkaline Earth			
Calcia	$CaO\cdot Al_2O_3\cdot SiO_2$	2138°	1170°
Baria	$BaO\cdot Al_2O_3\cdot SiO_2$	2282°	1250°
Magnesia	$MgO\cdot Al_2O_3\cdot SiO_2$	2471°	1355°
Strontia	$SrO\cdot Al_2O_3\cdot SiO_2$	2552°	1400°

3 Silica-alumina-flux eutectic points for various metal oxide fluxes. The ‘a’ on the end e.g. potassia denotes an oxide e.g. potassium oxide. The eutectic point is the lowest-melting combination of materials. *Phase diagrams by Henry Bloomfield.*

melting occurs over a range of temperatures. Potters usually mix silica, whiting, feldspar, and clay to make a transparent stoneware glaze. These melt together gradually, each oxide reacting with the other oxides, so alumina reacts with silica to form mullite; calcia reacts with silica to form wollastonite; alumina, silica, and calcia together form anorthite (calcium feldspar) (2). The precise eutectic melting point only occurs once the minerals anorthite, wollastonite (calcium silicate) and tridymite (high-temperature quartz) have formed. The lowest melting point occurs only when these minerals are mixed together in certain proportions. This eutectic is shown on a ternary phase diagram, with three axes instead of two. The contour lines show temperature, the lowest being at the eutectic point. Many stoneware glazes use several fluxes to give a better melt, including sodium, potassium, and calcium (3).

If the glaze has excess calcia, magnesia, baria, or strontia, it will no longer be at the eutectic composition and will not be transparent, as the excess will either remain unmelted or recrystallize on cooling. The glaze surface will be matte.

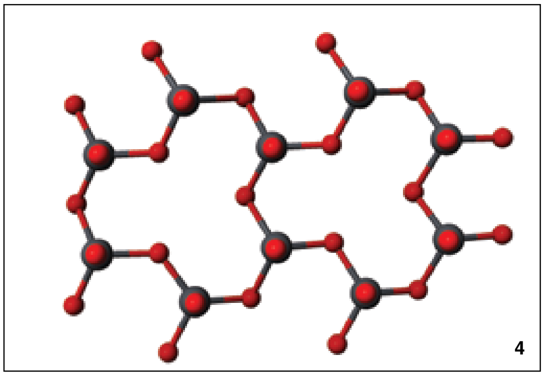
Silica Phases

As quartz is heated up, it changes in structure. The silica tetrahedra arrange themselves at slightly different angles to each other. The different forms are called phases. The silica phases include alpha-quartz (up to) 1063°F (573°C), beta-quartz (up to) 1598°F (870°C), tridymite (up to) 2678°F (1470°C) and cristobalite, which eventually melts at 3110°F (1710°C) to form amorphous liquid silica. Tridymite and cristobalite each have their own alpha and beta phases. In the high-temperature beta phase, the bond angles between Si-O-Si are slightly straightened out. Once the silica has melted, the bonds are broken and the structure becomes disordered and is no longer crystalline.

If molten glaze is cooled quickly, the silica will stay amorphous and disordered like in a liquid. However, the clay body may still contain some crystalline silica and this will undergo the reverse phase transitions on cooling. The crystalline silica in the clay body not chemically combined in kaolin or feldspar is known as free silica. The solid silica crystals change volume when they change from one phase to another at a specific temperature. Each silica phase has a slightly different volume, and potters need to be aware of the inversion temperatures as they can cause dunting in the kiln.

Quartz and Cristobalite Inversions

The two silica inversion temperatures important to potters, particularly when cooling the kiln, are the quartz inversion from beta to alpha at 1063°F (573°C) and the cristobalite inversion at 439°F (226°C). The quartz inversion involves a 1% volume change and is a gradual change. The cristobalite inversion causes a sudden 3% volume change and can cause dunting if the kiln is opened at this stage. However, the cristobalite inversion can be useful in preventing crazing in glazed earthenware. This is known as the cristobalite squeeze as it contracts the clay body and compresses the glaze. Earthenware clay bodies can withstand this stress but not stoneware, particularly ovenware which may be repeatedly heated to above 392°F (200°C), so cristobalite is not desirable in stoneware clay bodies. Fluxes in the clay body such as calcia and magnesia act as catalysts in the conversion of quartz to cristobalite. In stoneware and porcelain, more cristobalite forms the longer the ware is soaked or re-fired to high temperature, above 2012°F (1100°C). This may cause cracking when, for example, large plates are re-fired. The clay body suddenly changes in volume, but the glaze does not, causing stress and cracking of the plate.



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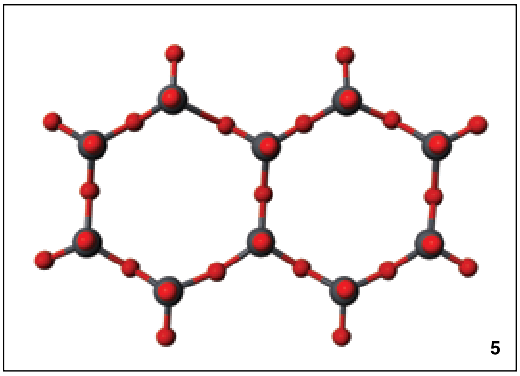

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4 Alpha quartz structure. Silicon atoms are gray and oxygen atoms are red. The Si-O-Si bonds are bent at an angle. *Diagrams by Elin Barrett.* **5** Beta quartz. At 1063°F (573 °C) the Si-O-Si bonds are straightened out, with an accompanying 1% increase in volume. *Diagram by Elin Barrett.*

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