Ancient Glazes

The beauty of a glazed ceramic arises from the interplay of light with the complex structure of the glaze. The methods of materials science reveal the ingenuity of ancient glazing technologies

by Pamela B. Vandiver

A glaze is the glassy coating that seals and adorns the surface of a ceramic body. Modern industrial glazes are usually colorless and transparent, as on a porcelain dish, or colored and opaque, as on a bathroom tile. But a visit to any art museum reveals that ceramic glazes encompass an immensely more diverse repertoire of visual effects. Blue faience glazes on ancient Egyptian amulets glow with intensity undiminished since the day they emerged from the kiln. Scenes rendered in red and black slip glazes spring to life on the sides of Grecian vases. Bright tricolor lead glazes, luminous celadons and dazzling porcelains speak to the taste and power of the Chinese imperial court.

Long before there were synthetic dyes and plastics, ceramic glazes offered artisans an unparalleled range of permanent colors and textures, which could be manipulated to satisfy a diversity of cultural demands. In most cultures, glazed ceramics were a prestige good—something that remained beyond the reach of common people because the necessary materials, know-how and manufacturing skill were often difficult to acquire. In 16th- and 17th-century Europe, monarchs collected Chinese porcelains so avidly that they sometimes risked bankrupting their treasuries. The European appetite for this “white gold” motivated prominent scientists to try to replicate porcelain during the early stages of the industrial revolution.

Today ceramic research focuses mainly on exploitation of the practical rather than the artistic possibilities of ceramics [see “Advanced Ceramics,” by H. Kent Bowen; SCIENTIFIC AMERICAN, October, 1986]. Yet the tools and strategies of modern materials science have also taken the study of ancient ceramics into a new era. Materials scientists study ways to process raw materials in order to create microscopic structures that will endow a ceramic with desired macroscopic properties, such as the ability to withstand extreme stress or temperature. Students of ancient ceramics approach the problem from the opposite direction: starting with a finished object, they try to determine the structures underlying its properties and to reconstruct the materials and processes that created it.

In our laboratory we have been studying the technological development of ancient glazes, which have not received as much attention as the ceramic bodies themselves. We study the archaeological context and utility of an ancient glaze, analyze its composition and structure and finally try to replicate it. We hope thus to answer a multitude of questions: What is the physical basis of the appearance of a glaze? What raw materials went into it, and how do these vary or constrain the glaze? What sequence of steps did the potters choose to develop? How were these procedures refined to produce a desired effect? The answers to such questions offer an intimate window on the thought processes of ancient potters and on the values of the societies in which they worked.

Ceramics are made of clays, which consist mainly of fine particles—less than 10 microns across—of aluminosilicates, which are among the most abundant minerals in the earth’s crust. The plate-like particles are stacked in layers, offering narrow interstices for water, which creates capillary forces that draw the clay particles together and allow them to slide past one another so that the clay can be plastically deformed.

When a clay is fired, the particles are sintered; that is, they melt just enough to make a glassy “glue,” which binds the particles into a rock-hard mass. The ceramic remains somewhat porous, however, because the clay is not heated high enough to melt completely; if it were to melt, the structure would collapse under its own weight. The porous body is therefore sealed by a glaze. Glazes are typically composed of fine, glass-forming particles, which melt and fuse to form an impermeable glassy layer after only a short firing at a relatively low temperature that retains the shape of the clay body.

Perhaps the best way to elucidate the melting behaviors of such ceramics as a glass or glaze is to contrast them with that of a crystal. In a crystal the atoms are stacked in orderly, three-dimensional arrays. The bond strength between like atoms in a crystal is uniform. Consequently, as a crystal is heated, the atoms vibrate at fixed sites in the array until they reach the melting point, when the thermal energy makes them abruptly disassemble into a more random, liquid state. A glass, on the other hand, contains impurities, called fluxes, that disrupt the arrays, giving rise to a random network analogous to the structure of a liquid. Because of the random arrangement and the variable bond strengths, glasses do not have a fixed melting point. When a glass is heated, it dissolves gradually, changing from the consistency of a solid to that of butter, then honey and finally syrup. By incorporating fluxes that have different bond strengths, one can manipulate the melting point and stability of a glass or glaze.

Although glasses and glazes are made of the same raw materials, such
as silica sand, lime, potash, borax and lead oxides, there are important differences between them. A glass in the making must be kept above the melting point for a long time, sometimes days, to ensure that all the raw materials melt, that no new crystals form and that trapped air escapes as bubbles or is reacted into the glass. A glaze, in contrast, cannot be held at peak temperature for long, because the clay body might also begin to melt.

Because glazes spend so little time at or near a high temperature, they often retain impurities, such as unmelted crystalline raw materials or gas bubbles. It is these impurities that dramatically alter the appearance of a glaze, making a clear glaze appear translucent or opaque, causing an inherently smooth surface to take on a satin, velvet or even oatmeal texture, and changing an optically flat surface to one having the same illusion of depth as jade and agate.

The appearance of a glaze results from the interactions of light with the outer surface of the glaze, with the interface between the glaze and the underlying body and with the substance of the glaze itself. The microstructure of the glaze is particularly important. Structures smaller than 100 microns lie below the limit of resolution of the human eye and so contribute to subtle textural effects. Structures of between 1 and 10 microns in diameter are near the visible wavelengths of light and so most strongly influence the optical properties and appearance of a glaze.

Light bounces cleanly off a smooth glaze surface (specular reflection), whereas it scatters off a rough surface. A matte glaze contains crystals that roughen the surface and scatter light in all directions. In Song dynasty Longquan celadons, the surface is slightly rough, embedded with quartz crystals measuring between 10 and 100 mi-
THERMAL HISTORY of glass, frit and two glaze types are shown here. Glass is held at a high temperature to melt impurities and allow bubbles to escape; while being formed, the glass may be reheated many times. A frit is sintered (partially melted) at a high temperature, cooled rapidly, ground into powder, applied as a glaze and refired at a lower temperature. Clear lead and feldspathic glazes are held at peak temperature briefly (A). To achieve translucency, the glaze is cooled slightly (B) to nucleate crystals and then held at a higher temperature for some time to allow the crystals to grow.

LEAD GLAZE

MATTE GLAZE

CEladON GLAZE

LIGHT interacts in different ways with different glazes. A lead glaze (left) is transparent and highly reflective. A matte glaze (center) has crystalline protrusions at the surface, which scatter light. A celadon glaze (right) contains quartz particles, bubbles and micron-size crystals, which bend and scatter light. A crystal layer at the glaze-body interface also reflects light.

crons, and reflects a combination of specular and diffuse light. Different glaze compositions reflect and absorb varying amounts of light. A soda-lime glaze reflects about 4 percent of the incoming light, whereas a lead glaze reflects about 8 percent, which gives a brighter appearance. Heavier elements increase both the refractive index and reflectivity of a glaze.

In a transparent or translucent glaze, light is absorbed, scattered and reflected at the interface between the glaze and the body. A smooth, white clay body will reflect a large amount of light and brighten the colors of the glaze, whereas a darker body will absorb more light and cause the glaze to appear darker. In celadons, crystals of anorthite, a calcia-alumina silicate, grow at the interface during firing; the white crystals mask the gray clay body and cause the blue-green glaze to appear brighter and more intense.

A variety of complex optical effects are generated within the glaze itself. Most obvious are the interactions that color a glaze. The simplest and most reliable coloring technique is to add a pigment, such as magnetite black and copper oxide red. More complex are colloidal colors, such as microscopic particles of gold, silver or copper; the particles produce colors by absorption, scattering and refraction.

The most subtle and interesting colors are often produced by yet a third means, a solution of transition-metal ions, which have outer electrons that absorb all but certain wavelengths of light. These ions include iron (which can produce colors ranging from yellow and green to brown and black), manganese (purple to brown), chromium (pink to green), cobalt (blue) and copper (green to blue) depending on concentration and oxidation state. These colorants can be tricky to use, since the energy level of their outer electrons is strongly influenced by the surroundings. Hence, copper is blue in an alkaline glaze but green in a lead glaze. If .5 percent of iron oxide is added to an alkaline glaze or glass, each iron ion becomes surrounded by oxygen atoms, and the resulting absorption pattern gives a Coke-bottle-green color. If a sulfur or carbon ion replaces one or more of the oxygens, the resulting color is a beer-bottle brown, because an iron-sulfur or iron-carbon pair absorbs more light across the entire spectrum.
Air bubbles also interfere with the path of light through the glaze. Bubbles may form because trapped air pockets expand with heat or aggregate as melting particles clump together or because salts in the raw materials decompose and release gases. If the glaze is allowed to melt to a fairly fluid state, most of the air bubbles rise to the surface and escape. But if the glaze remains viscous, the bubbles are trapped, much like bubbles in pumice. Large numbers of bubbles brighten a glaze, because the smooth interfaces between air and glass offer many reflective surfaces.

In addition to colorants and air bubbles, another important feature of the glaze is the presence or absence of crystalline particles. If a glaze or glass consists of .5 percent by volume of fine particles, less than a micron in size, it appears translucent, not transparent. If the concentration exceeds about 10 percent by volume, the glass or glaze appears opaque. The crystals may have a higher index of refraction than the surrounding glass, in which case light bends as it passes into a crystal and traverses a longer path through the glaze, creating an illusion of greater depth. If the index of refraction of the crystal is much greater than that of the glass, light bends by such a large angle that the glaze becomes quite opaque.

Artisans over the millennia have exploited these structural variations in glazes to create an amazing array of visual effects, including those that mimicked precious metals and stones. Ceramics could be plastically formed, usually with less effort than more precious materials, and could assume a greater diversity of shapes and sizes than metal or stone. These possibilities elevated glazed ceramics above mundane functionality to the status of luxury goods. To satisfy their patrons, artisans exercised considerable ingenuity in manipulating glazes. Ceramic glazes, then, offer an exceptional glimpse of ancient technology and its interplay with cultural values.

The earliest types of glazes in the New World, Southwest Asia and China were slips: suspensions of very fine clay particles in water, often with an added flux of a salt or ash. Slip glazes are fired for a short time at a low temperature, between 600 and 1,000 degrees Celsius. They melt only partially and so remain permeable. As early as 5500 B.C. potters in northern Mesopotamia had discovered that the color of a fired clay could be controlled by adjusting the furnace atmosphere. The variable agent is iron oxide, an abundant impurity in earthware clays. An oxygen-rich kiln atmosphere maintains the iron oxide in its red, hematite form (Fe₂O₃), whereas a smoky, oxygen-depleted atmosphere reduces iron oxide to black magnetite (Fe₃O₄). Both conditions arise in ordinary hearth and kiln fires, and so people would have observed the coloring effects and then learned to manipulate the firing to achieve them on purpose.

Slip-decorated wares reached their apogee in the Attic vases of the sixth second centuries B.C. Illitic clays mixed with water were left standing so that coarse particles would settle out. The finest clay and hematite particles remained suspended and were laded out. This slip was painted on the areas to be rendered black. The wares were fired in a smoky atmosphere so that the iron oxide over the entire surface was reduced to a black color. In the process the fine-particled slip glaze sintered into a glossy surface, whereas the coarser clay body remained largely unsintered. At the end of the firing and during cooling, more oxygen was vented into the kiln, causing the exposed, porous clay areas to reoxidize to a red color. On the other hand, very little oxygen could diffuse into the sintered slip, and so the glazed areas remained black.

Slip glazes everywhere were variants of this general style and shared the drawback of being too permeable. We recently identified a notable exception to this rule in a ware recovered from the site of Godin Tepe in western Iran. Known as Seh Gabi painted ware and dated to 3500 B.C., it was made from a calcareous, cream-colored clay and was decorated with a glassy black glaze. Our analysis showed that the glaze has the composition of a slip but had been fired at a higher temperature (1,050 degrees Celsius) and for a longer time than the body, which was fired at 800 degrees Celsius. This could have been done only if the glaze had been fritted, or preheated, at the high temperature and then ground up, mixed with water, applied to the clay body and refired at the lower temperature. This technology was short-lived; it was transmitted neither to subsequent generations nor to other areas. Seh Gabi remains the sole known example of a high-temperature clay-based glaze before 1500 B.C., when stoneware glazes appeared in China.

The first truly glassy glazes in the Near East developed from the stone—

LONGQUAN CELADON VASE from the 12th century is among the finest ceramics ever made. Bubbles and quartz particles, seen in cross section (top right), give the glaze luminosity and depth; the sea-green hue comes from a slightly reduced state of iron in solution. A scanning electron micrograph (bottom left) shows a quartz particle and needles of anorthite, which scatter light.
worker's art rather than from the potter's craft. These were the turquoise- and lapis-like blue faïences of Egypt. Around 4000 B.C. stoneworkers discovered they could create a stonelike material by shaping a gritty paste of crushed quartz debris, a sodium or potassium flux, some crushed limestone or malachite and water and then drying and heating it. A copper salt was added to the paste, which, together with the other fluxes, would effloresce onto the surface; when fired, the efflorescence would melt and form a translucent, blue, glassy coating. A second method, found from around 2300 B.C., involves firing quartz-based objects buried in a powder of copper salts, quicklime and charcoal; the salts vaporized and fused onto the surface to form the glaze. This technique may still be used in Iran to make beads. Faience artisans also developed a third group of techniques in which glazes were fritted, powdered and applied to quartz-based bodies.

The technological history of this important craft is complicated in Egypt, especially during the early stages. As the technology spread to—or was re-invented in—other regions of the Near East, differences in technique arose between regions and even between objects ascribed to a single workshop.

Around 1500 B.C., about the time Egyptian artisans first began making large quantities of glass beads and vessels, they also started incorporating powdered glass into quartz-based bodies to make decorative inlays for furniture and architecture. This development expanded the palette of colors from the traditional blue-green, dark purples, brown and black to include yellow, lime green, cobalt blue, violet and orange. Artifacts from Roman times indicate that Egyptians applied these frit glazes to tan-colored clay objects; these glazes appear glassier and duller and lack the gemlike quality or function of faience.

It is of interest to note that prefritted glazes have been reinvented in modern times as a way to eliminate defects such as bubbles and unmelted particles. Such glazes also solve the problem of possible toxicity from lead glazes, which, when incompletely melted, contain unreacted lead oxides that can dissolve into mildly acidic foods such as orange juice. A prefritted glaze ensures that the lead particles are completely melted and locked into a silicate glass structure. The stoneworking and faience-making traditions in the Near East, then, developed a glaze technology that differed from that of slip glazes, one offering a wider range of colors and a high gloss. For historical and cultural reasons, faience, frit, glass and glaze were reserved for imitating precious materials and for architectural decoration—artifacts that supported the ruling class. Glassy glazes could have also been developed to decorate and seal clay pottery, but they were not needed for these purposes, because other methods, such as slip decoration and impermeable resinous coatings already sufficed.

One reason slip glazes were firmly entrenched in the Near East was because clays in the region are of a pyrophyllite type suitable only for low-fired earthenware. These clays are difficult to work and are often found in seabed or riverine deposits that vary in composition. Clay with enough limestone have poor refractory properties: if fired at the range of 800 to 850 degrees C, they crumble easily; if fired at 1,100 degrees C, they will be more stable but will then warp, blister and eventually melt. What is more, kiln structures made from the poor clay cannot withstand repeated high firings. The quality of raw materials, together with the social and historical setting, constrained the technology and fixed the mindset of artisans. Hence, glossy pottery glazes made from such materials as limestone did not appear until Roman times.

In China, in contrast, potters enjoyed an abundance of excellent refractory clays and materials that enabled them to elevate ceramic technology to an art equal to painting and sculpture in the West. The analysis of Chinese glazes by our laboratory and by Chinese scientists reveals a gradual but continuous pattern of innovation in which new materials were employed for glazing and in which processes were invented or refined to produce new visual effects.

The chief driving forces of innovation in Chinese glaze technology were two: the early achievement of firing temperatures above 1,000 degrees C and the discovery of glaze stones—nonclay minerals such as limestone and "China stone" (a partially weathered mix of sericitic clay and quartz) that can be used to concoct a high-firing glaze. The first achievement can be credited to the thick loess deposits, in some places hundreds of meters deep, that blanket much of China. The loess consists primarily of quartz and so has a high melting point, which makes it a superb material for high-temperature kilns. To build a kiln in China, one had only to dig a chamber in a hillside, tamp the walls and create a vent to the surface. By 1500 B.C. pottery was often high fired at between 1,100 and 1,200 degrees C.

The idea of glaze stones might have come from observing the results of overfiring slip glazes containing clay, limestone and mica; deposits of ash from the kiln fire might have served as a flux for embedded particles of glaze stone. By the second millennium B.C. Chinese potters were using two types of glazing stones: limestone and China stone. Ground China stone formed the clay body itself, a process that culminated around A.D. 600 with the invention of porcelain, which was then predominantly of China stone. Kaolin, now the most common ingredient, was added only later.

By the 11th century A.D. artisans in northern China were supplying the imperial court with extraordinary wares such as the laverder-and-blue Jun ware and Ru ware, whose color was described as "blue sky after rain." Jun ware illustrates an unusual way to create an unctuous, stonelike texture. The glaze was allowed to sit at a temperature of about 1,250 degrees C and then cool slowly, forming an emulsion of two glassy liquids. Like oil and vinegar, the two liquids are more stable by themselves than they are in a mixture, so that they form a myriad of tiny globules some tens or hundreds of nanometers in diameter. The two glass phases have different indexes of refraction, causing light to bend as it crosses from one phase to another; the longer, more indirect light path creates the illusion of translucence and depth. The same effect appears in a shingingly shaken bottle of oil-and-vinegar salad dressing: the individual liquids are clear, but the emulsion is translucent.

In 1127 the Song court fled south and established the Southern Song dynasty in Hangzhou. Potters began a crash research program to adapt the local Yue folklore to the court's taste for lustrous, jadelike wares. The results of this effort were the celebrated Guan ("imperial") celadons and Longquan celadons. Longquan was a market town southwest of Hangzhou, where celadons were made primarily for export. The remarkable accomplishment of celadon glazes is their translucency, silky texture ranging in hue from pale sea green to gray-green.

The starting point for the celadon artisans were the Yue glazes, which are homogeneous, thinly applied clear glazes colored by iron oxide in shades
DIVERSITY OF GLAZES reflects variation in materials and processes. Fifth-century B.C. Attic wine cup (1) was decorated with a black slip over a red ground; a scanning electron micrograph shows sintered slip particles above a coarse clay base. Egyptian faience (2) is a glasy glaze over a ground-quartz body. Shown here are a superb chalice (800–900 B.C.) glazed by melting copper salts that had effloresced from the body; beads replicated in the author’s laboratory by firing them while buried in copper salts, quicklime and charcoal; and an inlaid design (about 1450 B.C.) made by mixing colored glass with the quartz paste. A two-foot-long lion (3) from the Temple of Ishtar in Nuzi, Iraq, dates to about 1500 B.C. and is the largest extant ancient ceramic with a glassy glaze. Bright lead glazes decorate an eighth-century Chinese jar (4). Lustrous “oil spots” on a Song dynasty tea bowl (5) are made by red hematite and yellow magnetite crystals. Intensely colored overglaze enamels (6) from the famille verte palette adorn an early 18th-century plate; the scanning electron micrograph shows the ultrafine hematite particles in red enamel. A Turkish Iznik tile (7) is decorated with vivid colors under a clear lead-alkali glaze.