

From Fermentation to Transportation: Materials in the History of Wine

The following article is based on a talk given by Stefan K. Estreicher (Texas Tech University) in *Symposium X on Frontiers of Materials Research at the 2002 Materials Research Society Spring Meeting on April 4 in San Francisco*.

"Penicillin heals men, wine makes men happy."

—Sir Alexander Fleming (1881–1955)

The Importance of Wine to the Ancients

In the Neolithic period (8500–4000 B.C.), *Homo sapiens* settled in villages, cultivated the land, and domesticated animals. These huge changes in lifestyle had important consequences. For example, living off cultivation implies saving seeds from one season to the next and protecting them from rodents and other threats: The first clay pots appeared during this period. Permanent communities also imply a risk of water contamination, a serious matter. Water-borne diseases (cholera, dysentery, and others) are still the most immediate threats facing populations displaced into temporary settlements by war or natural disasters. Today, water is filtered, boiled, or chemically decontaminated, but in Neolithic times, making water safe to drink must have been a major preoccupation. The answer was wine.

Beer and wine are both very ancient beverages, but wine is special. It is produced only once a year, in the fall, when the grapes are mature. Beer can be brewed at almost any time. Furthermore, if the grapes have enough sugar, natural fermentation can produce 12%, 13%, maybe even 14% alcohol, which is three or four times more than beer.

The amount of alcohol in wine is enough to kill many harmful bacteria, particularly in water. The ancients used wine to make water safer to drink. For millennia, wine was consumed mixed with water. In ancient Greek law, as codified by Zaleucus of Locris (~650 B.C.), it was written, "If anyone drinks unmixed wine without a physician's prescription, the penalty is death." This is 30 years before Draco of Athens and "Draconian law." The ancient Greeks always mixed wine with water, sometimes even seawater. In 58 B.C., Julius Caesar invaded Gaul and wrote of being stunned that the Celts drank unmixed wine. Even today during the Catholic Mass, the priest mixes wine and water—a symbolic gesture that dates back to Neolithic times.

The importance of wine to the ancients is illustrated by the number of gods associated with it. Everybody is familiar with

the Roman god Bacchus (Dionysus to the ancient Greeks). But the *Oxford Dictionary of Ancient Deities* lists 36 gods associated with wine. They exist in all of the ancient civilizations around the Mediterranean basin. In Roman mythology, Bacchus was born out of the thigh of Jupiter. This is something very special, and it was a virgin birth. In the Qur'an, the gardens of paradise are described as "a similitude of the Garden which those who keep their duty [to Allah] are promised: Therein are rivers of water unpolluted, and rivers of milk whereof the flavor changeth not, and rivers of wine delicious to the drinkers, and rivers of clear-run honey" (Surah 47.15). Clean water and wine, found in the same sentence.

Clay jars and amphorae were used for wine for over 5500 years.

But wine was much more than a healthy beverage. The alcohol in wine made it a powerful antiseptic. Various types of wine were recommended by physicians to treat a wide range of ailments. Hippocrates of Kos (460–375 B.C.), the father of medicine, even advised that "infants should be...given their wine diluted and not at all cold." He then specified which type of wine should be given to infants. Wine was also a social drink as well as a trade commodity.

When and how the first wine was made is unknown. However, it is impossible to cultivate grapes and not end up making some kind of wine. Yeast grows on the skin of grapes. If mature grapes are squeezed into a jar, the yeast transforms the sugar in the juice into alcohol and carbon dioxide. After a couple of days, there is wine. At the Neolithic settlements in the Zagros Mountains of today's Iran, wine was likely made from the native *Vitis vinifera sylvestris* grape. This species has male and female plants, with a few self-pollinating hermaphrodites. Farming led to the elimination of male plants that do not produce fruit, then of female plants that are no longer pollinated, leaving high concentrations of hermaphrodites. Over time, this cultivated grape evolved into *Vitis vinifera vinifera*, to which all European grape varieties belong. Concentrations of hermaphrodite pips found at a dozen sites throughout the Middle East are archaeological proof of vine cultivation.

Only Clay

Clay jars have been used for fermenting, storing, and transporting wine since the earliest times. Note that wine might also have been kept in animal skins or wooden barrels this early, but such organic containers did not survive long enough to be found by archaeologists.

To date, the most ancient archaeological proof of winemaking, even of wine technology, comes from the Neolithic site Hajji Firuz Tepe (5400–5000 B.C.) in the Zagros Mountains. A couple of decades ago, six balloon-shaped clay jars were found, each about 2 gallons in capacity. The chemical analysis (by Fourier transform infrared absorption spectroscopy) of the residue in the jars showed the presence of tartaric acid and its salt, calcium tartrate. Substantial concentrations of tartaric acid are only found in wine. The tiny crystals are often visible at the bottom of a glass of (a few years' old) wine. They look like grains of salt. Another residue in the jars was the resin from the terebinth tree, *Pistacia atlantica*. The insides of the jars were coated with it. While waterproofing might have been one consideration, it was certainly not the only one. The resin from the terebinth tree has antibacterial properties, and its presence slows the oxidation of the wine.

Partially or fully coating clay jars with resin (especially from the terebinth tree) was done systematically for as long as clay jars were used for wine storage, which was until the fall of Rome in the fifth century A.D. The ancient Greeks and Romans coated only the neck of their jars, while the Egyptians and more ancient civilizations often coated the whole interior. Today's only remnant of this practice is the Greek Retsina wine: Resin of *Pinus halepensis* is added to the must for flavoring. The Greeks rarely drink this wine; it is for tourists.

Clay jars in which wine had been stored have been found at numerous sites throughout the Near East. They contain tartaric acid and are coated with resin. About 700 jars were found in Abydos, a few hundred miles south of the Nile delta, in the tomb of one of the earliest rulers of Egypt, known as Scorpion I (~3150 B.C.) and assigned to Dynasty 0. These jars have a characteristic shape. They are long and slender and have a pointed tip that allows them to be partially buried in sand for storage. Their walls are thick, almost an inch, and they are stoppered with clay. Inscriptions on some clay stoppers describe the type of wine, its production date and region, and the name of the

winemaker—the kind of information found on modern wine labels. These jars are amphorae, an Egyptian invention that was widely used by the Phoenicians, Greeks, and Romans, with only minor changes in shape over the centuries. The Romans also used a much larger jar called a *dolium*, with a capacity of some 300 gallons, for storage and mass transport.

The amphora is a brilliant and technologically advanced device. It is simple, cheap, and it works. Clay is found almost everywhere, and an amphora is easy to make. Its inside is partially or fully coated with resin. It is easy to store and ship, and wine can be aged in amphorae for a long time.

The Egyptian winemaking technique is illustrated on the walls of a number of tombs. The workers pick grapes, which are crushed by foot. The must is poured into amphorae, which when full are plugged with clay stoppers. Small holes in the neck of the amphorae allow the carbon dioxide to escape during fermentation, at the end of which the holes are sealed with clay, and the wine can age, sometimes for decades. The wines from Falernum, on the southern slope of Monte Massico (about halfway between Rome and Pompeii), and Surrentium (south of Pompeii) were praised by many Roman authors. The Falernum wines were sometimes aged for as long as 30 years.

Clay jars and amphorae were used for wine for over 5500 years. Wine was fermented, stored, aged, and transported in clay: a single material for everything. We do not know how these wines tasted. But there is no doubt that different types of wines existed. The Egyptians had red as well as white (or rosé?) wines, and the Greeks produced everything from light, acidic white wines to the powerful “black” wines of Kos. These wines are described by physicians such as Hippocrates. The Romans produced cheap wines for the masses (including the common soldiers, who probably drank something akin to vinegar), but they also produced long-aging sweet wines that were celebrated by emperors and poets alike. Clay was a highly successful material in winemaking for a very long time. Suddenly, it disappeared.

Only Wood

Julius Caesar invaded Gaul in 58 B.C. For the first time, the Romans moved away from regions easily accessible by ship. Now goods such as wines had to be transported over land. With few or no roads, pulling a cart loaded with amphorae across bumpy terrain was a sure way to break the jars. The local population, the Celts, had solved this problem and developed the use of barrels made of pine

wood, with a typical capacity of 7 gallons. Caesar wrote very little about wooden barrels. The Latin word for such a barrel, *cupa*, is found only once in Caesar’s writings, and not in conjunction with wine. However, Caesar’s arrival in Gaul marks the time when the Romans encountered wooden barrels.

In Italy, alcohol was considered *quintessence*, literally the fifth element, something important enough to rival air, water, fire, and earth.

The Celts were not the first to use wooden barrels. About 500 B.C., Herodotus described barrels of palm wood used for the transport of wine from Armenia down the Euphrates and Tigris rivers. The technology used to build waterproof wooden ships is not very different from that used to make wine barrels. But palm wood is very hard to bend, and manufacturing tight barrels must have been difficult. I am not aware of any references to wooden barrels used for wines by the ancient Egyptians or Greeks, but the Romans certainly adopted them in the first couple of centuries A.D. Wooden barrels gradually replaced amphorae, and by the beginning of the 5th century, the latter were no longer produced. For a long time, wine would be fermented, stored, and transported in wood.

The Roman Empire fell to the Barbarians in the middle of the 5th century. A period of intermittent wars followed. Without a central authority, law and order, chaos ensued. In Western Europe, the Church represented an element of stability. Emperor Constantine had converted in 313, and Christianity had become the official Roman religion a little later. By the time of the fall of Rome, the Church had established a hierarchy and a strong organization, with monasteries and land. When King Clovis and his Franks (the barbarians who ended up dominating much of what is France today) converted in 496, the Church gained political power and maintained it until the French Revolution of 1789. However, the Church did not favor much technological innovation or scientific inquiry, even in relation to winemaking. The first half of the Middle Ages was not a happy period for wine.

To make wine, the grapes were simply crushed by foot and the must was poured into wooden barrels. Only the wealthier monasteries had (wooden) wine presses. Foot-treading was done in the open air—

possibly to avoid carbon dioxide poisoning. Throughout the process, the young wine was exposed to a lot of oxygen. Unless the barrels were kept full to compensate for evaporation (or consumption), the wine turned to vinegar within a few months at best. The price of a six-month-old wine was half the price of a younger one. There is a French saying, still in use today: “*Quand le vin est tiré, il faut le boire*” (when wine is drawn [from a barrel], it must be drunk). The technology was primitive and did not allow the decades of aging that the Egyptians and Romans achieved with simple amphorae.

From the fall of Rome until the Renaissance, the Arabs became the guardians of Western civilization. They kept the ancient texts and developed science, medicine, and technology. Throughout the Middle Ages, new knowledge arrived in Western Europe from Islam (and China). The Arabs maintained glass-blowing skills and, around 700, invented distillation. Alembic (*al-anbiq*) and alcohol (*al-koh'l*) are Arabic words.

Distillation allows one to extract the essence from flowers or fruits, but wines and other fermented juices can be distilled as well. The process is based on the difference in the evaporation temperatures of water (212°F) and alcohol (172°F). One evaporates the alcohol and condenses the vapors. Late in the 11th century, crusaders returning from the Middle East brought with them the art of distillation. The production of nearly pure alcohol revolutionized medicine. In Italy, alcohol was considered *quintessence*, literally the fifth element, something important enough to rival air, water, fire, and earth. The technology quickly spread. In Germany, distilled wine was called *Gebrandtwein* (burnt wine), which became the Dutch *brandewijn*, the origin of “brandy.”

In the late 11th century, the Cistercians arrived in Burgundy. They were quality fanatics, going as far as to taste the soil before deciding where to plant vines. They developed the best vineyards and produced much better wines than in the preceding 600 years. They knew that wine barrels must be kept full and that it was best to store them underground, in cellars, away from temperature fluctuations. The first large wine cellars were built during this period.

In the mid-12th century, Aquitaine (the region around Bordeaux) became famous again. It was known as a wine-producing region for a couple of centuries after the Romans established a harbor and planted vineyards there, but then, nothing: There are precious few mentions of Bordeaux anywhere during the first half of the

Middle Ages. This changed following the marriage of Eleanor of Aquitaine to the future King Henry II of England in 1153. Suddenly, the wines from Bordeaux became the focus of a huge trade with England. In Old English, a cask used to store wine was called a *tun*. The word soon referred to the weight of the cask when full, and the capacity of ships became measured in *tuns*, the number of casks of wine they could carry. The capacity of ships is still measured in tons today.

The English lost the Hundred Years' War and Bordeaux in 1452, but the reputation of Bordeaux wines remained strong. The English became more active in Portugal, in particular in the Douro Valley from where Port wines emerged in the 1600s. In the 1500s, the Spanish brought vines to Central and South America. In the mid-1600s, the Dutchman Jan Van Riebeeck planted the first vines of South Africa, in Constantia, just south of Cape Town.

Many important events related to wine occurred in the 1600s. The beneficial effect of a fungus, *Botrytis cinerea* (the "noble rot") was discovered by accident and the Tokaji Aszú was born ("aszú" refers to the dry, rotting grapes, or the "aszú paste"). The word Aszú on a wine label implies that some fraction of blend in the bottle is noble-rot wine. The diarist Samuel Pepys was the first to mention a brand-name wine: On April 10, 1663, he recorded that "[at the] Royall Oake Taverne in Lumbard-street [London], I drank a sort of French wine called Ho Bryan that hath a good and most particular taste that I never met with." This was Château Haut Brion. Until then, wines had generic names such as "Claret," "French," "Spanish," or simply "red" or "white." Note that the same Pepys was president of the Royal Society in July 1686, when he put his name to the imprimatur of Newton's *Principia*.

Wood and Glass

The first thick and sturdy glass bottles of the type needed for wine were manufactured in the 1630s by Sir Kenelm Digby in Gloucestershire. The timing coincides with the first coal (or rather, coke) furnaces. These early furnaces could not be used for making wrought iron, for the coke contained too much sulfur, causing the iron to become brittle. The first coal furnace practical for producing wrought iron was designed much later, in the 1750s, by Abraham Darby II. But glass could be made. The first glass bottles arrived in Porto and Champagne—to the delight of Pierre Dom Pérignon, who strove to make quality still (not bubbly)

wines in Champagne. These bottles mark the end of wood as the single material in winemaking. For some 1200 years, the presses had been made of wood and the must had been poured into wooden barrels or casks where it would ferment. Wine was kept and transported in barrels, and drunk from barrels. Suddenly, and for the first time in the history of wine, *two* materials were used: Wines could be fermented and matured in wood, then bottled in glass for aging, thus protected from oxygen.

The early wine bottles of the 1600s were designed to stand, not lie down.

The art of glassmaking is very ancient. The Egyptians knew how to make glass as early as the second millennium B.C. The technology is closely related to metallurgy. Both involve furnaces and molten material, and glass consists of silica (sand) plus metal. The Egyptians discovered that trace amounts of specific metals produced glass of various colors, for example, gold for red and cobalt for blue. They imported cobalt from Persia for that purpose and created sophisticated glass containers. They covered a clay shape with frit (bits of solid glass), heated it, and removed the clay after the glass solidified. The Phoenicians invented glass blowing around 100 B.C. and mass-produced glass cups for wine. The Romans made glass windowpanes, vases, and decanters. However, because of impurities in the raw materials, this glass was not clear. It was also not strong enough for storing wine.

The first truly clear glass was produced in the 15th century on the Island of Murano, just off of Venice. This achievement involved very pure source material, high temperatures maintained for long periods of time, and temperature control during cooling. This glass, called *cristallo*, was also fragile.

The early wine bottles of the 1600s were designed to stand, not lie down. Since they were blown, each was slightly different in shape, thickness, and capacity. Many people bought bottles personalized with a seal such as a heraldic crest, a name, or simply initials. A wine merchant would fill the bottle directly from his barrel. Later, and for a long time, bottles were produced by blowing molten glass into metal molds. The first molded bottles were produced by Ricketts of Bristol in 1821. The mass production of cheap bottles of uniform shape and capacity was an American invention

by Michael J. Owens (1859–1923). His first fully automatic bottle-making machine was built in 1903. An improved version (1912) could produce over 50,000 bottles a day. The last two Owens machines stopped operation in 1982.

From roughly 1650 to 1950, (good) winemaking involved two materials: wood (barrels) for the fermentation, maceration, and maturation, then glass (bottles) for storage.

Stainless Steel, Wood, and Glass

In the early 1960s, stainless-steel tanks began to be used on a large scale in California. These tanks, made of low-carbon steel with up to 10% chromium (by weight), ranged in size from 1,000 to 250,000 gallons. The breakthrough was temperature control, but there are other advantages.

First, in a barrel, it is very difficult to control the temperature during the fermentation and to continuously mix the skins with the juice. Stainless-steel tanks are easily fitted with temperature controls (including jackets through which a refrigerant is pumped, thermostats, and computerized controls that maintain the desired temperature to within a couple of degrees), and internal stirring components. Second, the level of wine in a barrel must be checked every couple of months and added to in order to compensate for evaporation. No such evaporation occurs through stainless steel. Third, the lifetime of a barrel is of the order of seven years, and the interactions (exchange of tannins, oxidation, and such) between a wine and its barrel vary with the age of the barrel. These issues do not exist with stainless steel. Fourth, barrels are hard to clean and difficult to keep free from unwanted bacterial growth, while stainless-steel tanks are easily cleaned. Fifth, not all types of wine benefit from barrel aging. A Cabernet Sauvignon or Chardonnay will improve from contact with wood, but a light Sauvignon Blanc will taste better without it. Steel tanks neither add nor take away flavors in the wine. Sometimes, winemakers put oak chips in the tanks to add wood tannin to the wine. These tannins tend to balance the harshness of the tannins from grape skins and seeds. They allow a wine such as a Cabernet Sauvignon to be drunk much younger (I much prefer to age my wines).

Thus, today's wine industry uses three materials for fermentation, maceration, storage, aging, and transport. The fermentation is done in temperature-controlled stainless-steel tanks, with or without maceration. The wine may (or may not) spend time in wood, up to two years. The precise amount of time, type of oak, and age of the

barrel are important factors in determining the characteristics of a wine. When ready, the wine is transferred into glass bottles.

Other Materials and Concluding Remarks

Many materials relevant to winemaking have not been discussed here. For example, *animal skins* have been used for a long time. They are still precious in situations where the must or wine has to be carried. The workers on the volcanic Island of Madeira still carry must in 11-gallon goatskins. *Stone* was the material of choice for foot-treading in regions where few or no trees grew. For example, stone *lagares* were used in the upper Douro Valley for foot-treading of grapes. These vats are about 4 m × 4 m and 80 cm deep. The large surface-to-volume ratio allows more tannins, anthocyanins, and color to be extracted from the grapes in a shorter time than in conventional processes.

Then, there are stoppers, in particular, *cork*. The best corks, punched out of the bark of the cork oak, come from Portugal. A cork oak is stripped of bark every 5–7 years. The piles of bark are left to dry for about one year, then the corks are punched, cleaned, covered with a thin silicone layer, and shipped. At present, a war is raging between those who like to use real corks in bottles and those who want to use plastic corks or screw-on metallic caps. Many wineries have switched from (expensive) Portuguese corks to all sorts of cheap stoppers, including composites of bits of low-quality cork glued together. The result was a much higher incidence of

“corky” wines (up to 10% of bottles are claimed to be tainted with a cork smell) and a call to replace all corks. My experience suggests that the accidental cork smell is very much less frequent. Quality corks in properly stored bottles have a very low incidence of corky smell or taste. Corkiness is (mostly) caused by a contaminant called TCA (2,3,6-trichloroanisole). Screw tops, now being used even for some very expensive wines, do not have that problem, of course. But nobody knows if a wine can age with such a stopper, how it will evolve over the years, and what unwanted odors might pop up. Although the processes involved in the aging of wine are not understood, many believe that the wine “breathes” through the cork. Contact with the tiny amounts of oxygen flowing through the cork might be just what is needed for the wine to age. Some ancient wines were aged for decades in thick clay amphorae—another material that is not airtight.

One may wonder what materials will be used for winemaking in the future. For over 5500 years, clay was king, then only wood was used for some 1200 years, then combinations of two (wood and glass) and three (stainless steel, wood, and glass) materials were involved. Will we discover that some vast improvement occurs with a fourth material? I doubt it, since this would complicate an already complex process and increase costs. Wooden barrels are already in danger of disappearing because they are expensive and require a lot of work. Barrel-aging is now done only for higher-quality wines.

Another material that might be replaced sooner or later is glass. Wine bottles are heavy and glass breaks. Some lighter look-alike material, classy-looking but light, cheap, and unbreakable, might be just around the corner.

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FOR FURTHER READING: P.E. McGovern, S.J. Fleming, and S.H. Katz, eds., *The Origins and Ancient History of Wine* (Gordon & Breach, Amsterdam, 2000); B.L. Vallee, “Alcohol in the Western World” (*Scientific American*, June 1998); H. Johnson, *Vintage* (Simon & Schuster, New York, 1989); wines in the Middle Ages are discussed in *Historia* (in French, vol. 73, 2001); J.L. Mass, M.T. Wypyski, and R.E. Stone, *MRS Bull.* **26** (1) (2001) p. 38; I. Amato, *MRS Bull.* **22** (12) (1997) p. 54.

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