

- Plenary Address -

**Wine and the Vine : New Archaeological and Chemical Perspectives
on Its Earliest History**

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This conference reminds me very much of the one we held on "The Origins and Ancient History of Wine" in the Spring of 1991 at the Robert Mondavi Winery in Napa Valley. That region is by all accounts the premier winemaking area in the States, and here we are in what is considered the best in Canada at the Cool Climate Oenology and Viticulture Institute, no less. At the Mondavi conference, we intermixed wine-tasting and talk with recent discoveries, just like we've been doing here for three days. During the week of conferencing in the Napa Valley, two wines flowed at every lunch and four at every dinner, and everyone went away with the sense that it would be difficult to ever duplicate it again. You could say that this conference has a broader perspective than the Mondavi conference, including sensory evaluation, marketing, and more of the nitty-gritty technology of winemaking, but the discussions have taken on the spirit--even the true ferment--of a Greek symposium, like what we enjoyed a decade ago. We should definitely do this more often!

I thought that what I might do this morning is give you an overview of some of the advances in our understanding of ancient wine over the past ten years. I will purposely focus on much of my own research using Archaeological Chemical techniques--or more romantically, Molecular Archaeology--since that is what I am

most familiar with but also because I believe that it holds out the best prospects of discovering much more in the future. And wine and winemaking is one of those few subjects that recognizes that the longer the time dimension, the better the product, and that digging up what others would consider esoteric bits about ancient winemaking might just might impact on how we make wine today and in the future. One has only to consider the introduction of French winemaking techniques, based on long tradition—whether ageing wines in oak barrels or fermenting on the lees—to imagine that as we learn more about ancient varieties and processing methods that other new vistas will open up.

I wish that I could offer you some wine or some Midas Touch, which I will describe shortly, to go with my talk—we have often done that at talks to illustrate the kinds of wines the ancients drank, but unfortunately I couldn't stuff enough bottles into my carry-on luggage and retsina is not yet being produced in the New World. So, we'll defer that for another time, although the Greek wine-tasting today may fill the void. My slides will hopefully help to bring the subject alive.

Molecular Archaeology—holds out the promise of opening up whole new vistas on the ancient world. Unlike textual, pictorial or ethnoarchaeological inferences, its power lies in providing direct, contemporaneous, non-tendentious evidence. In the last several decades, highly sensitive instruments have become available that are capable of detecting milligram, even microgram quantities of ancient organic materials. This graphic of a Molecular Archaeologist at work in his laboratory nicely summarizes the situation that the aspiring practitioner in this field faces. Here, we have a Mycenaean kylix, a beautifully contoured vessel of superb craftsmanship, and we want to track down the ancient organics that it originally contained. Contemporaneous frescos show that the vessel was used for drinking or libation, but what was being drunk or poured out? And, if we can determine

what it contained, what does this say about ancient cuisine, social and religious practices, and possibly much more? Much has been said and written about pottery typology, but hardly anything is known about what the vessels were actually used for.

Porous earthenware pottery, made from aluminosilicate clays, is able to absorb the ancient organics, especially in liquid form, and hold them relatively intact for centuries, even millennia. That's not to say that there hasn't been degradation with time, that some organics have been washed out from the pottery (perhaps when an archaeologist runs them through an acid bath) or that there's modern contamination, but the prospects are now very good for tracking down the natural source—whether plant or animal—for the organic compounds that are identified.

The star of the show at our 1991 Mondavi conference was this rather nondescript pottery jar, dated to about 3500 B.C., which at the time was the oldest chemically confirmed wine jar in the world. Here, I'm presenting the jar at a press conference at the winery, together with Virginia or Ginny Badler, who first noted the reddish residue on the inside of the jar. Intriguingly, this jar was excavated by a Canadian team from the University of Toronto and Royal Ontario Museum at a site in the central Zagros mountains of Iran. So, if you want to get a glimpse of the actual vessel, you just need to travel to the museum up around the lake. Ginny accompanied the jar on its trip from Toronto to Napa. The jar paid full fare and was strapped into a first-class seat; it was one of the most undemanding customers ever flown by the airline, and Ginny even got to enjoy an extra meal and drink that the jar refused.

After the Mondavi conference, I was on the look-out for even earlier evidence of

wine. At the Mondavi conference, we had already entertained the idea that Paleolithic man or woman might have serendipitously discovered wine from time to time. One might imagine a Palaeolithic people foraging in a river valley, at some distance from their cave. They are captivated by the brightly colored wild grapes with their tart and sugary taste. They gather up as many of the berries as possible, perhaps into an animal hide or even a wooden container which has been crudely hollowed out. Depending on their ripeness, the skins of some grapes rupture and exude their juice, under the accumulated weight of the grape mass. If the grapes are then left in their container, gradually being eaten over the next day or two, this juice will ferment, owing to the natural yeast "bloom" on the skins, and become a low-alcoholic wine. Reaching the bottom of "barrel," our imagined caveman or woman will dabble a finger in the concoction, lick it, and be pleasantly surprised by the aromatic and mildly intoxicating beverage that has been produced accidentally. More intentional squeezings and tastings might well ensue. The likelihood, however, of finding preserved organic residues inside leather or wooden containers to confirm this hypothesis, are obviously very small. Moreover, whatever wine was made during this period, must have had a very restricted production schedule, only during the Fall when the grapes matured (a kind of Beaujolais nouveau, Austrian *Heuringe* or perhaps they were smart enough to wait until the first frost and make an ice wine), and must have been drunk quickly before it turned to vinegar).

If winemaking is best understood as an intentional human activity rather than a seasonal happenstance, then the Neolithic period in the Near East, from about 8500 to 4000 B.C., is the first time in human prehistory when the necessary preconditions for this momentous innovation came together. Neolithic villages were the first, permanent, year-round settlements, which were made possible by domesticated plants and animals, such as cereals and ruminants. With a more

stable base of operations and an assured supply of food, what might be termed a Neolithic cuisine emerged. A variety of food processing techniques--fermentation, soaking, heating, spicing--were developed, and Neolithic peoples are credited with first producing bread, beer, and undoubtedly an array of meat and cereal entrées that we continue to enjoy today. Minor crafts, which are important in food preparation, storage and serving, advanced in tandem with the new cuisine. Of special significance for winemaking, pottery and plaster vessels first appeared around 6000 B.C.--here's the Neolithic wine jar that took winemaking back to 5400 B.C. The plasticity of clay made it an ideal material for forming shapes, such as vats and narrow-mouthed storage jars, for producing and keeping wine. After firing the clay to a high temperature, the resultant pottery is essentially indestructible, and its porous structure helps to absorb organics.

After the 1991 Mondavi conference, I was on the look out for any Neolithic wine specimens. What better place to look than our own University of Pennsylvania Museum, which has one of the best collections of well documented excavated artifacts in the world. Two years ago, I asked the Dr. Mary Voigt if she had ever noted intriguing residues on any of the Neolithic pottery she had excavated. In 1968 she had directed an expedition to Hajji Firuz Tepe, and the recovered artifacts were divided between the government of Iran and the museum. Now a professor of anthropology at the College of William and Mary in Williamsburg, Virginia, Voigt still directs the Gordion excavation in Turkey for the museum and visits us several times a year. Yes, she told me, she did remember yellowish residues on several sherds from Hajji Firuz. At the time, she had thought the residue might be from milk, yogurt or some other dairy product. An analysis, however, had come up negative. The sherds then sat in the Near Eastern storage room in the museum's basement for twenty five years.

After I questioned her, Mary "re_excavated" this sherd, and our investigation began in earnest. About four inches long and two inches wide, the sherd was covered with a thin yellowish deposit. According to Voigt, the deposit had covered the only the lower half of the vessel as reconstructed. Six such jars of the same shape, each with a volume of about 9 liters (two and a half gallons), had been set into the floor of what appeared to be a kitchen in a mud_brick building at Hajji Firuz, dated to ca. 5400-5000 B.C. (here we see Mary in red shirt and white Panama hat excavating the room). The use of the room in which the jars were found as a kitchen was supported by the finding of numerous pottery vessels which were probably used to prepare and cook foods, together with a fireplace. The overall layout of the structure, which was well-made and not unlike modern village houses in the area today, was approximately square; a large living room, which may have doubled as a bedroom, "kitchen," and two storage rooms might have accommodated an extended family.

Chemical analysis enabled us to resolve the archaeological puzzle of what the jars originally contained. Using the organic chemical techniques that we have developed to analyze wine residues--infrared spectrometry and liquid chromatography--we examined the yellowish deposit of the Hajji Firuz sherd. One organic compound, in particular, is characteristic of wine, occurring in large amounts only in grapes: tartaric acid (this is a chemical formulation of the molecule, which occurs as the L-+ form in nature but can be transformed to the other stereoisomers by shifting the hydroxyls and hydrogens to other locations in the molecule, which is arranged in a tetrahedron fashion).

Just to give you one example of the type of data that we look at, here you see the infrared absorption spectra of the Hajji Firuz yellowish residue, together with that of synthetic calcium tartrate as a modern reference sample and two other ancient

wine samples from early cities in southern Mesopotamia (Susa) and in Egypt (Abydos). All the ancient samples clearly absorb infrared light at a frequency of 1720 cm^{-1} , which is characteristic of tartaric acid. In addition, the calcium tartrate, which forms from tartaric acid in the calcareous geological environment of the Near East, is present, as shown by the broad absorption in 1610 to 1560 cm^{-1} range as well as additional absorptions at 1420 cm^{-1} , 1380 cm^{-1} , 1280 cm^{-1} , etc. (here, we see crystals of calcium and potassium tartrate which form in wine over time and constitute the lees or dregs). The presence of tartaric acid and its calcium salt in the Hajji Firuz jar indicates that the jar contained a grape product.

Some archaeological considerations now come into play in determining that this grape product was in fact wine. Note that the jar has a relatively long, narrow neck, which is ideally suited to pouring liquids. I have already said that the residue was confined to the bottom half of the jar, and this is where precipitates from liquids accumulate. Most likely, then, the jar contained grape juice. A warm climate and slow pressing methods assured that grape juice quickly fermented to wine, since natural yeast lives on some grape skins. Here, we see the carbon dioxide escaping from the wine as the grape sugars are fermented to alcohol—a seemingly miraculous evolution that must have captivated early winemakers, as it rocked their fermentation vessels back and forth and especially when they experienced the mind-altering effects of their finished product. Fermentation had probably even begun before the jar was filled, because of slow pressing methods in antiquity and high temperatures in the Middle East.

Of course, if oxygen remains available, fermentation can continue and eventually the acetic acid bacteria convert all the wine to vinegar. This is something that any competent winemaker, even one living in the Neolithic period, wants to avoid. Although cork was not yet available, raw clay stoppers function the same way,

absorbing liquid and expanding to seal off the mouth of the jar. Such stoppers were found in the vicinity of the wine jars at Hajji Firuz.

Another chemical constituent of the Hajji Firuz residue, which acts as a preservative, made it virtually certain that the jar originally contained wine. On the infrared spectra, this component is marked by absorptions at frequencies of 2900 and 2850, which cannot be explained by tartaric acid or its calcium salt (which have no absorption in this range). Absorptions at these frequencies are characteristic of hydrocarbon compounds, which are comprised essentially of only hydrogen and carbon. In this case, the ultraviolet absorption spectrum using our liquid chromatograph provided us with the identity of the unknown component. It most closely matched the spectrum of terebinth tree resin, which is dominated by a group of polycyclic compounds called triterpenoids (this one--moronate or moronic acid--has a name that is especially striking).

The terebinth tree (*Pistacia atlantica*, a member of the pistachio family) is widespread and abundant in the Middle East, occurring even in desert areas, and a single tree, which can grow to as much as 12 meters in height and 2 meters in diameter, can yield up to 2 kilograms of the resin in late Summer or Fall, just about the same time that the grapes are ready to be picked (this is a tree growing in Turkey, with ripe fruit). Today, the resin is still used to make chewing gum and perfume in the Middle East. Although our word "turpentine" actually derives from the word "terebinth," the natural resin, unlike the concentrated distillate, is not offensive in taste and smell.

Pliny the Elder, the famous 1st c. A.D. Roman encyclopedist, devoted a good part of book 14 of his *Natural History* to the problem of preventing wine turning to vinegar. Tree resins--pine, cedar, frankincense, myrrh, and very often, terebinth

which was known as the "queen of resins"--were added to Roman wines for just this purpose.

Tree resins had been a standard treatment for wounds and as internal medicine for centuries by the ancient Egyptians, Assyrians, Greeks and others. Their triterpenoid content (diterpenoids in the case of pine resins) prevent bacteria from growing, since they act as anti-oxidants, using up the oxygen that the bacteria need. Without any knowledge of bacteriology, the ancient winemaker simply applied the pragmatic observation that tree resins were useful in curing human disease to develop a medicine for the dreaded "wine disease," which causes wine to go to vinegar. The most famous and expensive tree resin additive to Roman wine was myrrh, which came from the Arabian peninsula and the Horn of Africa (this is a tree growing in Yemen). This resin even has an analgesic effects, so that if the desired goal of preventing the wine from becoming vinegar failed, at least one's senses were numbed. However, myrrh and other exotic tree resins, like frankincense, were generally unavailable to Middle Eastern cultures before the 700 or 800 B.C. and the rise of camel caravaneering, and our Neolithic winemaker had to be content with terebinth tree resin.

But to return to some additional chemical findings that we made. A second reconstructed jar from the "kitchen" at Hajji Firuz, which was still complete and displayed in the Tokens-to-Tablets gallery of the University Museum, was taken off exhibit for photographing by a syndication group who flew in specially from London at the time of discovery. Because of the difficulty of taking objects off exhibit and getting permission to carry out chemical analyses on them, this was my first opportunity to examine this jar in detail. I immediately saw a reddish residue in patches on the lower inside of the jar. Tests were carried out, and this residue also proved to be a combination of calcium tartrate, with relatively more

tartaric acid, and terebinth tree resin. Whether or not this is a red wine, to go with the white ("yellowish") wine of the first jar analyzed, can only be determined by identifying the red anthocyanin (cyanidin) or yellowish flavonoid (quercetin) that also degrade to characteristic organic acids, such as gallic acid. Such polyhydroxy or polyphenolic aromatics are important, because they also serve as anti-oxidants, like the tree resin constituents, to scavenge free radicals, thereby lowering cholesterol and protecting humans against cancers and other ailments. These are some of the good compounds in wine that have been receiving so much attention of late (including resveratrol).

It is not known whether the Hajji Firuz wine was made from the domesticated (*Vitis vinifera vinifera*) or the wild grape (*sylvestris*). The site lies within the ancient and modern distributional zone of the wild grapevine, as established by pollen cores from nearby Lake Urmia; this zone is indicated in purple on this map, together with other sites, generally dated between the 6th and early 3rd millennia B.C., that have yielded grape remains, indicated by the grape cluster, or wine jars, marked by the jar symbol. Although wild grapes were available once a year in the Fall, the wine in the jars might well have been produced from a precursor of the highly successful domesticated type. The quantity of wine in the "kitchen"--about 50 liters (14 gallons) if all six jars contained wine and were nearly full--does suggest fairly large-scale production and consumption, especially for a household. If the same pattern of usage were shown to exist across the whole of the Neolithic stratum, only part of which was excavated, it might be concluded that the grapevine had already come into cultivation.

What is truly amazing, though, is that more than 7000 years ago, resinated wine was already being produced and stored in these jars. In upland regions such as Hajji Firuz, where the wild grapevine and the terebinth tree grew together and

produced their fruit and resin about the same time of the year, mixing these products together might have occurred accidentally or as a result of an innovative impulse. However it happened, Neolithic peoples must already have had an appreciation of the preservative and medicinal properties of tree resins. And the use of wine and tree resins continued to expand, until it dominated the pharmacopeias of later, literate civilizations.

If we were really daring archaeological chemists, we might have done what 19th c. chemists actually did--scrape out some of the residue inside the jar and add water. Although the alcohol and aroma are long gone, we might be able to detect the terebinth resin and have the honor of drinking the oldest, best-aged vintage in the world, even if it is *retsina*.

For the ultimate origins of wine and viniculture, one will probably have to look farther north and at higher elevations where the wild sub-species thrives, and other conditions for the development of winemaking are met. The wild grapevine grows today throughout the temperate Mediterranean basin, along the shores of the Black Sea and the Caspian Sea, and in some drier regions of the Near East and Central Asia. Somewhere in this vast region, it can be argued that the single wild Eurasian grapevine was taken into cultivation, and eventually developed as our domesticated type (*Vitis vinifera vinifera*), which today is the source of almost all the world's wine and a seemingly infinite number of varieties (such as Chardonnay, Cabernet-Sauvignon, and Merlot). I will be coming back to the possibility of multiple domestications shortly.

The Neolithic communities in the upland regions of the northern Zagros Mountains, the Taurus Mountains of eastern Turkey (here we see a vineyard laid out in the foothills of Mt. Ararat), and the Caucasus Mountains were well-

established from an early date, and are excellent candidates for early winemaking and viniculture. The paintings of Pirosmani, a primitivist Georgian artist of 19th-20th c. highlight the importance of viniculture, winemaking and wine-drinking in this region (showing vineyards, marani in which the wine was aged, drinking horns, and wineskins). Unfortunately, few sites in this ethnically diverse and politically divided region have been excavated, let alone published in a western language. Despite the difficult political climate, I was fortunate to travel to Georgia and Armenia in 1998, and collect pottery from some of the earliest Neolithic sites, dating between 6000 and 5000 B.C., like this jar sherd from Khramis Didi-Gora. The applied motif here is especially interesting, because it may well show a celebrant dancing beneath a grapevine. Although we are yet to publish the analyses, these jars also contained a resinated wine.

The domesticated vine's advantages over the wild type can be traced to its hermaphroditism in which the male stamens and female pistil occur together on the same plant; this self-fertilizing plant, which was then selected for larger, juicier and tastier fruit and fewer seeds, can be cloned by transplanting branches or roots (in addition to typical white and red domesticated grapes, this slide also shows the red mare's nipple of Central Asia on the left).

Tantalizingly, grape pips of the "domesticated" type (which are elongated and narrow, as contrasted with the broad, short wild type) are reported from Chokh in the Dagestan Mountains of the northeast Caucasus, dating to the beginning of the 6th millennium B.C., and from Shomutepe and Shulaveri along the Kura River in Transcaucasia, belonging to the 6th through the early 4th millennium B.C. I was able to bring back samples of these—the viniculturalist Revaz Ramishvili said it was like parting with his soul—and together with other ancient Egyptian material and modern wild and domesticated grape varieties from Greece and Turkey,

collected last year, a far-flung ancient DNA study is in progress. I am collaborating with the University of California at Davis (Carole Meredith and Jose Vouillamoz), and the Universities of Geneva, Madrid and Ankara (Francois Lefort; José Miguel Martínez Zapater; Sabit Ağaoğlu, Ali Ergül and Sümer Aras). Much more work on these and other finds are needed before their significance for the prehistory of winemaking can be determined.

The genetic "history" encoded in the genomic and mitochondrial DNA of modern wild and domesticated grapes, together with that of any available ancient samples, suggests an another way to track the development of viniculture in the Old World. Using recombinant DNA techniques, it might be possible to delimit a specific region of the world and the approximate time period when the wild grape was domesticated. Like the Eve hypothesis, which claims to trace all of humanity to an original mother in East Africa on the basis of mitochondrial DNA lineage trees, a Noah hypothesis would seek the progenitor of modern domesticated grape varieties and their sequence of development and transplantation. Noah, the biblical patriarch and "first vintner," is said to have planted a vineyard on Mount Ararat after the flood, with dire consequences when he drank the fermented beverage (Genesis 9) (painting by Giovanni Bellini, 1430-1516 A.D.).

Of course, this scenario goes counter to a recent poster at the San Diego conference (Animal and Microbe Genome X/1st International Grape Genome Project Workshop, 12-16 January 2002), under the names of my collaborators and myself, which argues that the DNA evidence from many modern European varieties shows the Eurasian grapevine was taken into domestication in more than one place. So which is it?: the Noah Hypothesis or multiple domestications? I think that the jury is still out, but as an archaeologist, I am quite naturally impressed by the gradual spread of wine cultures radiating out from the northern

mountainous region of the Near East to Egypt, to Greece, to Italy, and the rest of Europe. I believe that it is more likely that the plant was domesticated in the Near East first and then crossed with wild plants throughout the Old World at various times. Eventually and with a lot more work, analysis of ancient grape DNA—ideally from the wood of the parent plant but possibly, too, from the offspring including seeds and skins—will provide a definite chronology and reconstruction of what happened.

In order to track these developments, my Molecular Archaeology Laboratory at the University of Pennsylvania Museum has become a kind of repository or cellar for ancient wine samples. I'll give you just one particularly fascinating example of what happened over and over again throughout the ancient world--the transplanted of the domesticated grapevine to the Nile Delta some 5000 years ago.

Archaeobotanical seed evidence shows that the grapevine had been transplanted to the Jordan Valley by at least 4000 B.C., where the wild species did not grow. The success of this experiment is memorialized in the story of Israelite spies bringing back gigantic grape cluster from the Holy Land (as seen here in a painting by the French artist Poussin).

The wild grape also never grew in ancient Egypt. Yet, a thriving royal winemaking industry had been established in the Nile Delta by at least Dynasty 3 (ca. 2700 B.C.), the beginning of the Old Kingdom period. And marvellous tomb paintings later illustrate the winemaking process--from picking the grapes, stomping them out, and fermenting the grape must or juice in sealed amphoras.

Is it possible to know when the first grapevines were transplanted to the Nile

Delta and how the royal winemaking industry was developed? Our understanding of the prehistoric background for the Delta industry leaped forward with the discovery of this royal tomb at Abydos on the middle Nile River, which is about 400 miles up the Nile, in the cemetery close to where the later Dynasty 1 and 2 pharaohs were buried. . One of the first kings of Egypt, Scorpion I, was buried here during Dynasty 0, around 3150 B.C., about 100 years before the unification of Egypt [by the pharaoh Narmer and the start of Dynasty 1].

The tomb was excavated by a team from the German Archaeological Institute in Cairo. It was dug 8' down into desert and is in the form of a model funerary house in which only 8" wide slits intercommunicate between the rooms. The burial chamber in the northwest corner held the remains of a wooden shrine (the sides of which are indicated on this top plan) where the king was laid out with his ivory scepter. The other rooms were stacked high with goods--beer jars, bread molds, stone vessels, possibly clothing, and so forth--to accompany and provide for the king in the afterlife.

The most interesting finding from my perspective were three rooms on the opposite side of the tomb from the burial chamber. Here, some 700 vessels had been piled up in 3 or 4 layers. These jars (here we're looking down onto one of the layers of jars) must have been dropped down into the rooms from above, after which the whole tomb was covered over with a roofing of wooden beams and clay and then a mound of sand.

As you can see, the jars were filled with sand when they were found. Once the sand was poured out from each jar, rings of a yellowish crusty residue were revealed on the interiors of the jars. The rings were slanted off from the horizontal, and are best explained as the remains of a liquid that had gradually

evaporated, with materials on the surface of the liquid agglomerating to form the rings. Some of the jars also contained something highly unusual that had never been seen before: figs had been sliced up and perforated to run a string through them so that they could be suspended from the mouth of the vessels into the liquid. The preservation of the strings and pulp of the figs, more than 5000 years old, is quite amazing. It is not attested for any other ancient wine, although it might well have served as a sweetening agent or special flavoring; by cutting up and stringing out the fig segments, more of the wine would come in contact the fruit.

It was again resinated wine, according to our battery of chemical analyses. That the jars contained a fermented beverage was confirmed by a recent DNA analysis of the yeast in the lees by researchers from the Universities of Florence, Harvard, and Berkeley (Drs. Mario Polsinelli, Duccio Cavalieri, and Robert Mortimer). Here is a shot of the microscopic culprit responsible for the fermentation of sugar to alcohol--*Saccharomyces cerevisiae*--in the process of reproductive budding. Fragments more than 800 base-pairs long were preserved, showing that the ancient winemaker was already making use of a precursor of *Saccharomyces cerevisiae*, which was to go on to become the principal wine yeast and variants of which branched off to yield the bread and beer yeasts.

With an average volume of 6 to 7 liters for each of the 700 wine jars in the tomb U-j wine cellar, the king could have drawn upon some 4500 liters (or almost a 1000 gallons) of wine in his afterlife. Where had such a large quantity of wine been produced? The extremely dry terrain of Abydos was an unlikely place to have transplanted the domesticated grapevine and produced wine. Some grape remains have been recovered from predynastic sites in the Nile Delta, but not nearly in the quantity that would point to mass production.

To find out where the wine jars came from, we turned to another tool of modern Molecular Archaeology: Neutron Activation Analysis (here we see the Brookhaven National Laboratory reactor out on Long Island, NY). In this method, small pieces of pottery from the wine jars are ground up and subjected to high-energy neutron beams. Characteristic gamma rays are produced by each radioactive chemical element, especially the so-called rare earths, and sophisticated statistical techniques are then used to make comparisons to a large database of other ancient pottery and modern clays from all over the Middle East, to determine if the clay used to make any given Abydos jar can be “chemically fingerprinted,” so to speak, to a specific region. The assumption is that the jars were made in the same places that the wine was.

The best stylistic parallels for the Abydos wine jars are actually with examples from sites in the coastal plain of southern Israel, the hill country around Hebron, the southern Jordan Valley, and Transjordan. And this is precisely the area that the Neutron Activation study confirmed as their origin.

The earliest botanical evidence for the domesticated grape in this region—as I said, dating to the 4th millennium B.C. or Chalcolithic period, which precedes the Early Bronze Age—is from the Jordan Valley. The grapevine had evidently been transplanted to this region from farther north, so that by the time of the Abydos tomb, it was being grown on a large scale throughout the southern hill country whose climate and terrain was ideal for growing grapes and producing wine.

Our combined study of where the Abydos were produced and what they contained is a good example of how archaeological chemistry is establishing trade routes of specific organic goods, wine in this case. It is now clear that the wine deposited in the tomb of the Dynasty 0 ruler at Abydos was transported some 500 to 700

miles, overland by donkey caravans, including the Sinai stretch (the so-called “Ways of Horus”) of ten days, and then probably by boat up the Nile.

What appears to be happening in the earliest stages of Egyptian history is that the rulers and upper classes begin to import wine as a costly, prestige item, not unlike what goes on today when we serve that special bottle of Opus 1 or a fine ice wine to friends. Once the beverage has established an economic foothold, usually being incorporated into religious ritual and social custom as well, the next logical step is to transport the grapevine itself, and begin producing wine locally to assure a more steady supply, at a lower cost and tailored to local tastes. The Nile Delta with its extensive tracts of irrigated land, sunny days and short rainy season was ideal, and became the focus of a royal wine industry in the first two dynasties. The wines of Tutankhamun of the New Kingdom, which were stored in these amphoras that have labels almost as detailed as those on modern wine bottles, were produced here. These labels indicate where the vineyard was located, sometimes the vintner’s name, the production date according to the year of the Pharaoh’s reign, and the kind or quality of wine (“sweet,” “good,” very good,” “very, very good”)—this an archaeological chemist’s dream come true, an ancient vessel whose date of manufacture, place of origin, and contents are known.

If I had more time, I could trace this gradual process of trade in wine and the establishment of new wine industries to southern Mesopotamia (where beer drinking through straws and more refined wine drinking in goblets is depicted on cylinder seals, such as this one in the University Museum’s Babylonian collection) and to Shiraz region of the Bacchic poets such as Omar Khayyam. Or we could travel west to Greece where Dionysos reigned supreme. For example, our chemical investigations of ancient Greek vessels revealed that a real revolution in beverage-making took place around 1500 B.C. In the grand palaces

of Knossos and Pylos, the ancient Minoans and Mycenaeans drank and libated a combination of resinated wine, barley beer and honey mead, a kind of Greek grog or toddy, you might say. This mixed beverage was amusingly portrayed in an article the *New Scientist*. What was even more strange—since we don’t know how this beverage was developed or introduced into Greece—a similar mixed beverage shows up around 700 B.C. in central Turkey. This was what was served at the “King Midas” funerary feast, which you may have already read about.

I’ve saved this example of ancient wine until last, because you will probably be able to relate to it better and it illustrates the tremendous potential of this newly emergent field. As I have been trying to show, the pay-off in Molecular Archaeology is when one makes a major break-through in developing methods to identify what can be called “finger-print” or marker compounds that can be traced to specific natural products.

Everyone’s heard of King Midas and knows about his “golden touch.” What people didn’t realize is that there was a real King Midas, and now using Molecular Archaeological techniques, we can actually take a step back in time and have been able to re-create, up to a point, what people ate and drank at a funerary feast of his or one of his predecessors shortly before 700 B.C.

I don’t know how many of you have been to central Turkey, but here we see the so-called Midas Tumulus, which stands over a 100’ high and dominates the site of ancient Gordion, the same capital city of the Phrygians where Alexander the Great cut the Gordion knot and became ruler of all of Asia.

The burial chamber, made of a double wall of logs and timbers, was deep down in the center of this enormous accumulation of soil and stones (located by drilling).

It is the earliest, intact wooden structure in the world, and it was excavated by the University of Pennsylvania Museum in 1957, under the direction of Rodney Young.

Here is what the king looked like when the Penn excavators broke through the wall--an amazing sight, like Howard Carter's first glimpse into Tutankamun's tomb. According to radiocarbon determinations and the tree-ring dates of the logs, as well as the style of the artifacts in the tomb, it can be dated to about 700 B.C. The Assyrians, who controlled most of the Near East at this time, mention that a king named Mita, Midas to the Greeks, ruled the Phrygians or Muski in central Turkey; Mita gave the Assyrians some competition until, after a few military defeats, he was brought in line and became an Assyrian ally. So, all the pieces of evidence--the huge tumulus, the tomb and its rich furnishings, the datings, the historical information of the Assyrians--make it likely that Midas was buried here. If not Midas himself, then it must be the final resting place of another wealthy Phrygian ruler.

At the feet of the excavators was the body, laid out in state on a thick pile of dyed textiles inside an unique log coffin. These textiles in fact show how remarkable the preservation conditions inside the tomb were. Although the body of the king had disintegrated, patterns of purple and brown dyes could be discerned, which unfortunately began to fade as soon as the tomb was opened to light and air. A sample of a textile brought back to Philadelphia, though, did yield indigo blue in an analysis carried out in my laboratory. And, of course, blue and purple are the colors of royalty.

In the background, you will see what is considered the largest, most comprehensive Iron Age drinking set ever found--some 157 bronze vessels.

Perhaps surprisingly, in view of Midas's legendary "golden touch," these vessels were made of bronze, not gold. Yet, once the accumulated layers of greenish oxidation were removed, the bronze gleamed like the precious metal, like this ram-headed situla or bucket.

The furniture, which has been extensively by Dr. Elizabeth Simpson of the Bard Graduate Center for Studies in the Decorative Arts, was equally well preserved, and represents some of the finest pieces from antiquity--such as this unique 3-legged walnut table with inlaid geometric patterns in juniper woods. Elizabeth noted that the furniture, especially the large log coffin, had originally been set up at the funerary feast outside the tomb, before it was disassembled and moved into the tight space of the tomb.

But, it wasn't just the furniture and the textiles that were preserved and could be reconstituted and brought back to life, as it were, by using the tools of Molecular Archaeology. The real gold, as far as I was concerned, was what these vessels contained. The ancient organic residues that you see inside these pottery jars constituted the left-overs of the main entree of the feast. They held the chemical clues, and there is no substitute for the actual physical remains of an ancient meal, even if the food has decayed and the beverage evaporated away. The jars were placed in three large cauldrons or vats after the beverage which they originally contained had been drunk or poured out as libations--I'll be coming back to the King Midas beverage later when we have dessert. The total amount of residue inside these jars that we had available to analyze--some 5 pounds--was extraordinary, especially when you consider that we can get good results with milligrams, even micrograms, of ancient organics. This was an embarrassment of riches for a whole range of tests, and still have lots left over for molecular archaeologists of the future.

I won't say too much about the main entrée—as our evidence showed, it was a spicy, barbecued lamb or goat and lentil stew. Specific fatty acids (caproic, caprylic, and capric), triglycerides, and cholesterol show definitely that the meat was goat or sheep (represented here by Dolly, the first cloned mammal, and her normal offspring, Bonnie). Just like the meat that you throw on the grill at home, the barbecuing produced what are called polycyclic aromatics (some alkyl phenol derivatives: phenanthrene and cresol. Since no bones were recovered from the residues, the meat must then have been cut off the bone. Lentils were the predominant vegetable in the stew (as suggested here in an adapted photo from a modern Mediterranean cookbook), as revealed by a plant steroid, chondrillasterol. Although some part of the meat and vegetables might have been sacrificed before the funeral banquet, as the Homeric epics and other ancient texts tell us, the lion's share of the ingredients were homogenized into a scrumptious stew for the royal funerary banquet, as shown by almost identical chemical results from all the analyses, no matter what pottery jar the sample was taken from. I don't have time to go into the chemical evidence for the other ingredients, but wine, olive oil and honey gave added flavor or were used in the marinating and basting process. The stew was then finished off with anise or fennel and other spices [possibly native bitter vetch or wild fenugreek]. For details, I would refer you to the Dec. 23, 1999 cover story in *Nature* magazine.

The beverage, which washed down the entree, is what I am most interested in telling you about this morning. Here is the marvelous lion-headed situla or bucket which, together with its ram-headed counterpart and other jugs, was used to transfer a beverage from three large cauldrons or vats (each with a capacity of about 150 liters or 33 gallons). The beverage was transferred to smaller cauldrons (mounted on the special serving tables of different inlaid woods), from which this

beverage was ladled into exactly 100 drinking bowls of the so-called omphalos or belly-button type. These bowls, without handles according to Near Eastern tradition, fit comfortably into one's hand for easy drinking. They are on the order of a quart—a fair amount to drink, although some of the liquid might have been poured out as a libation before the feast proper began. For those with a greater thirst or status, a half-gallon variety was also available, such as this replica bowl with swivelling ring handles. We can see how such vessels were used in antiquity from the stone reliefs in the palace of the Assyrian king, Sargon II, at Khorsabad (714 B.C.), with attendants dipping their lion-headed buckets into large cauldrons and taking the beverage to Sargon's associates who raise their lion-headed drinking-horns high.

What did these vessels contain? Our chemical investigation of the intense yellowish residues inside the vessels (I brought a small sample with me) has shown that the beverage was a highly unusual mixture of wine, barley beer and honey mead, a kind of Phrygian grog, along the lines of Minoan ritual cocktail but not resinated (to which some of you will express a sigh of relief). Wine was again marked by the principal organic acid in grapes—tartaric acid—and its salts.

My laboratory has also dabbled in barley beer, having identified the earliest brew based on the chemical evidence. It was inside this wide-mouthed jar from the Zagros Mountains of Iran, dating back to about 3500 B.C. The jar had unusual criss-cross incisions on its interior which were filled with a yellowish residue. This residue proved to be so-called “beerstone” or calcium oxalate. The name “beerstone” suits the compound, because it settles out from barley beers and accumulates at the bottom of the fermentation vat. It is a very bitter—even poisonous compound—so it's a good idea to eliminate it from the brew. Since beerstone was detected in the residues of the King Midas beverage, barley beer

must have been part of the mixed fermented beverage.

The final ingredient is mead, the famous Viking drink, which was held high and imbibed from drinking horns. Mead is fermented honey, which was one of the few natural sources of simple sugars in ancient times (long before our processed sugar beet or cane). Honey is made only by bees (this one here is the well-known European honey bee (*Apis mellifera*), embedded in 25 million-year-old amber). Bees also produce beeswax. Although the sugars rapidly break down, the components of beeswax are very well preserved and are virtually impossible to filter out from any honey product such as mead. Distinctive beeswax compounds were present in the King Midas beverage residues, showing that mead was also part of the grog.

To get a handle on how such a beverage might have been made, we then engaged in what is called experimental archaeology—you learn about an ancient technology by trying to replicate the process today.. I provided the ancient recipe to a number of wine and beer makers, and have then “reverse-engineered” and brought the beverage back to life. The best known example is “Midas Touch,” made by Sam Calagione of Dogfish Head Brewery in Lewes, DE., which is now available commercially. Other more wine-based interpretations are now in preparation on Crete. I happen to think that grapes and wine were crucial to the fermentation process in particular, and probably predominated in the finished beverage.

To illustrate the process, I’ll use the beer version by Sam as an example. Such a mixed beverage may sound extraordinarily strange, and wine connoisseurs may well turn up their noses at Midas Touch. But, it has been extremely well received, and its aromatic qualities are especially appreciated by the female of the species.

Beyond the basic ingredients, there were many processing decisions that went into “re-creating” this beverage. One of the most important considerations was whether each beverage—the wine, the beer, and mead--was made separately and then mixed together at the end of the process, or whether all the ingredients were thrown into the pot, beehive and all with lots of added nutrients, and fermented en masse from the start. We opted for a single fermentation, although the beehive was replaced by a delectable, filtered honey made from the herb thyme. Among other considerations, there was the question of whether or not to let the natural yeast of the grapes and honey take their course, as was probably done by the Phrygian brewer. We decided to help this process along by adding a dry mead yeast. Yellow muscat was chosen as the grape varietal, since it has been shown by DNA analysis to be related to the earliest cultivated grapes in the Middle East.

One issue could not be resolved by our chemical analysis. No bittering agent was detected, but it was clearly needed to offset the sweet honey, grape sugar, and barley malt. Hops were ruled out, since they were only introduced several hundred years ago in northern Europe. In keeping with the golden look of the residues and the Midas touch, I decided to use yellow saffron, a native Turkish spice gleaned from the female stigmas of the crocus flower (the three orangish or reddish filaments seen here). Some 5000 flowers are needed to produce 1 ounce of the spice, so it’s no wonder that it’s one of the most expensive spices in the world—one ounce can cost as much as \$300 or \$4800/pound. It has a wonderful fragrance and a distinctive, slightly bitter taste. It even has an analgesic effect. Just what was needed to finish off the delectable potion, a golden-hued drink, with reddish highlights, truly “fit for King Midas.”

The decomposed body of the king, lying in state in his coffin, might be viewed as the just reward for his over-indulgence. Yet, a (physical anthropological) study of

his skeleton showed that he lived to the ripe old age of 60 or 65, far exceeding the average life expectancy of the time. Here's a reconstruction of his head based on an examination of his skull by forensic scientists, and it gives you an idea of what Midas might have looked like in life.

You might be left with the impression that these ancient people were real boozers, having a range of fermented beverages to choose from. But, besides the pleasant psychotropic effects when not drunk in excess, fermentation actually preserves and enhances the nutritional content of foods. More importantly, people who drank alcoholic beverages, as opposed to straight water, in antiquity had a better chance of surviving--the alcohol and anti-oxidants killing any harmful microorganisms--and thus reproducing.

Contrary to legend, the king in this tomb--if he is indeed Midas--does not appear to have starved as a result of his "golden touch" or to have poisoned himself to death as legend would have it. One of the curses of having a golden touch, for instance, is that your food and wine change to molten gold, which is hard to digest. If his funerary feast reflects what he ate and drank in life, however, Midas benefitted from a high-protein diet and a bracing fermented beverage.

I hope that these few remarks will have given you a glimpse into the marvelous world of ancient wine. The domesticated grapevine and winemaking was eventually carried to many other parts of the world--Greece, Rome where select wines were produced in the 1st c. B.C, to southern France (here the Roussillon region near the Pyrenees along the Cote d'Azur), and up the Rhone and Rhine Rivers. Today, of course, large parts of southern Europe are planted with the vine. And from there, it is spread out to the New World, which actually had numerous native wild species, as recognized by the Vikings who called it

Vinland, like this *labrusca*. Strangely, the native Americans never used this wealth of grapes to make wine, perhaps, because they are too "foxy" or sour.

Napa Valley (the vineyards of the Robert Mondavi winery are seen here in the background) and now other regions of the New World, like here in Ontario, have done extremely well with the domesticated Eurasian species, whether Chardonnay, Pinot Noir, or Cabernet Sauvignon. We have come full circle--almost every New World wine, with their infinite varietal range of tastes and bouquets, ultimately derives from the Eurasian species of the northern Zagros and Caucasus transplanted again and again. A truly remarkable story of a truly remarkable plant and its product intertwining itself with social customs, religion, and economies throughout the world.

Fermented beverages are especially important in understanding human innovation and cultural/technological development. Except the Eskimos and the native peoples of Tierra del Fuego, humans have shown a remarkable propensity to develop independently alcoholic beverages from any available sugar source. By reconstructing more and more of how each people accomplished this feat, we may re-discover the unique climatic conditions that gave rise to the earliest varietal grapes. We may discover by ancient DNA analysis eventually what natural yeasts are best for producing the most interesting flavors and aromas for certain grapes. Some labor-intensive procedures of antiquity--like stomping grapes with one's feet so as not to damage the skins and introduce too much tannin or individually selecting grapes for certain qualities--still have their place, and who knows, other ancient methods of winemaking may again come to the fore. The use of ice, for example, may or may not have been applied to making wine, but it was certainly important in its enjoyments--Chinese and Roman emperors brought down from the mountains to their capitals and had special coolers made to hold their wines

through the hot, humid summers.

Once again, I would like to thank you for having me here this morning as a speaker. I hope that I have whetted your appetite for Molecular Archaeology and Wine—they are the perfect metaphor or paradigm for exploring much more of our heritage, whether it be our genetic development, cuisine, medical practice and various arts and crafts, to understand them better and even bring them back to life.

Note: To see the images referred to please go to these web sites:

www.sas.upenn.edu/~mcgovern/

www.sas.upenn.edu/museum/Wine/wineintro.html

www.sas.upenn.edu/Midas/intro.html