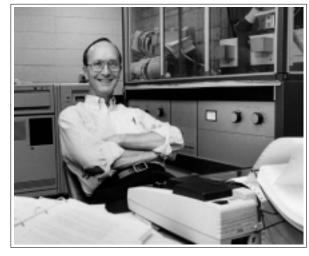# THE 2004 EDELSTEIN AWARD ADDRESS

THE DEEP HISTORY OF CHEMISTRY

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Introduction

Chemistry began long before Dalton or the alchemists, and even long before the earliest written chemical records such as those of the Roman, Pliny the Elder. In fact, chemistry was an essential component in the emergence of the human race and the development of human culture. These events took place during the last million years, reaching a climax in Southwest Asia some five thousand years ago.

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In the development of human culture, physics preceded chemistry, if one defines tool making as involving the principles of physics. In 1949, Kenneth Oakley of the British Museum argued that tools in essence made our ancestors human (1). He argued that the process of tool making aided the evolution of a larger brain. Humans, however, are not alone in the physical processing of tools. Although many animal species use tools, their production almost always is controlled genetically. Nonetheless, learned, as opposed to genetically hard-wired, use of tools is not infrequent in the animal kingdom. Otters break open shell fish with rocks and crows drop bones from a height to open them. Some birds have proceeded to the next higher step, of manipulating the raw materials, as in adjusting the length of a stick to rout out insects from a log or nest.

The earliest example of tool making by hominids (human-like animals in general, now often called hominins) at present is considered to be the altering of stones. Softer materials such as wood may have been worked previously, but the artifacts have not survived. Relatively sophisticated stone working by hominids (compared with the accomplishments of any non-hominid species) goes back at least 2.6 million years, the date of a site in Ethiopia (2). The species associated with this site is from the genus *Australopithecus*, an ape-like animal that preceded our genus *Homo*, for which the earliest date is 2.4 million years ago. Thus the physics of tool making was known to a very distant, pre-human ancestor.

The First Chemical Reaction

When did chemistry begin? The controlled production of fire was the first chemical reaction carried out by hominids. This discovery set hominids even further apart from other animals. Although a few species have made and worked crude tools, no other species has been able to create and control fire. If tool making set pre-hu-

mans on the road towards humanness (although other factors may have been at least as important), fire making confirmed, refined, and expanded the process, possibly helping to define the evolutionary moment when our ancestors became human. We became the first and only chemical animal. The control of fire had profound repercussions on our species. It provided protection and warmth, allowing our ancestors to migrate into cold climates and people the earth. Its light allowed them to extend their productive hours beyond daylight, expanding social interactions and helping the development of culture. In due course, fire was used to process food by stabilizing, tenderizing, and sterilizing it and possibly enhancing its taste. Such processing moves beyond survival strategies and becomes a cultural motif. Cooking itself of course is a chemical process. Another chemical process requiring fire was tool enhancement through annealing. Stone tools were hardened through heating tens of thousands of years ago. Finally, technologies utilizing fire ("pyrotechnologies") eventually included the production of ceramics, metals, and glass, as is discussed in later sections.

The earliest evidence for fire is controversial. Objects out of context may have been burned or charred for any number of reasons. The most unequivocal evidence then is the discovery of a hearth. The very presence of a hearth implies that humans were well advanced in the control of fire. The earliest such evidence may be at Terra Amata, located on the French Riviera, dated to at least 230,000 years ago (3). Humans living at this time were either very early examples of *Homo sapiens* or the predecessor species *Homo erectus*. Strong claims (but not a hearth) have been made for controlled fire at the site of Gesher Benot Ya'aqov in Israel, dating to 790,000 years ago, from the discovery of burned seeds, wood, and flint (4). Controlled fire was inferred from the pattern of distribution of these materials. The hominid species prevalent at that time was either *Homo erectus* or *Homo ergaster*. Observations at the even earlier site of Swartcrans Cave in South Africa and at a similar site in Kenya dating to 1-1.4 million years ago have been interpreted in terms of fire generated by hominid ancestors, either *Homo habilis* or *Australopithecus robustus* (5). The older evidence, however, is more controversial.

It is safe to conclude that some time between 230,000 and a million years ago, humans or their immediate ancestors had figured out how to create, control, and propagate fire as a tool, providing the many advantages described above and thereby making them chemists.

The Next Steps

The physical evolution of the modern human was almost complete by 100,000 years ago. Mental capabilities, as judged by the size and shape of the cranium, also were almost indistinguishable from that of modern humans. The extent of self consciousness in these peoples, however, is unknown. The development of speech undoubtedly was the critical step in establishing full humanness. This step required a modern larynx, not possessed by the Neandertals (*Homo neanderthalensis*). Speech arose as a means of communication possibly as early as 80,000 years ago but certainly by 35,000 years ago, probably in Southwest Asia and soon thereafter in Europe (6). Already before language, humans had employed a number of chemical processes and materials in addition to fire in its support roles.

(1) Cooking of food began more than 100,000 years ago, probably the result of observations on wildlife killed by natural fires (7). Although cooking is a chemical process, it is very complex and not easily attributed to one or more chemical reactions.

(2) Heat from fire also was used to improve the workability of flint and other stones, as early as 50,000 years ago. Heating stone up to about 350ºC prior to working improves its knapping and flaking properties. Heat treatment causes a color change in the stone as the result of molecular alterations, which may be studied by electron spin resonance spectroscopy (8).

(3) Natural pigments, particularly red ocher (hematite, or Fe_2O_3) were exploited by humans more than 100,000 years ago (9). Both Neandertals and Cro-Magnon peoples used such materials in burial or fertility rites. By 30,000 years ago, humans were grinding minerals to produce such pigments without chemical processing. In addition to reds and browns from red ocher, they obtained yellow from yellow ocher, black from soot or manganese dioxide, and white from calcined bone or white clays such as kaolin. These pigments were employed in the extraordinary cave paintings in southwestern Europe that date to more than 30,000 years ago (10).

(4) The chemical repertory of humans expanded into petroleum products. Bitumen was obtained from natu-

ral sites, of which the La Brea Tar Pits in Los Angeles is probably the most familiar to American audiences. Neandertals at the Mousterian sites of Umm el Tlel and Hummal in Syria left stone tools with bitumen residues that presumably had been used as adhesives as early as 36,000 years ago (11). Processing of bitumen involved mixing it with other materials to create something not readily available in nature: real chemistry. The addition of calcite ($CaCO_3$), silica (SiO_2), or gypsum ($CaSO_4$) to bitumen makes asphalt. Both pure and processed bitumen saw increased use in Mesopotamia from the residents of Jarmo in Iraq (7000 B.C.), the 'Ubaids (from 4500 B.C.), the Sumerians (from 3000 B.C.), the Babylonians (from 2000 B.C.), the Assyrians, and the Akkadians (12). These materials were used not only as adhesives but also as sealants for houses and boats and even as building materials. The Babylonians probably represent the high point of construction with bitumen, either as a constituent of bricks or as an adhesive between them, to construct roads, palaces, dams, bridges, sewers, and the famous ziggurats now in Iraq. Extant writings by Nebuchadnezzar II (ca. 630-ca. 561 B.C.) describe the use of bitumen in the Tower of Babel (the word being the Hebrew corruption of the name Babylon).

Synthetic Stone

Aside from the reworking of stone and food with fire, the aforementioned uses of chemical materials involved only physical, rather than chemical, processing. Thus, pigments were gathered from the environment but not altered chemically; bitumen was harvested from natural sources and possibly mixed physically with gravel. The working of stone, wood, bone, and other available raw materials involved physical processing only, albeit sometimes highly complex or artistic. In all these cases (except cooked food and heat-treated stone), the product clearly possessed the same chemical makeup as the raw materials.

What then was the most likely first example of human qua chemist? It may well have been the invention of plaster, to provide a manipulable substitute for stone. The very earliest suggestion of such a material occurred in the Sinai Peninsular at the site of Lagama North VII. At around 14,000 years ago, the inhabitants attached stone tools to handles by means of plaster. The invention of lime plaster has been attributed to the Geometric Kebaran culture of North Africa and Southwestern Asia during the Mesolithic or Epi-Paleolithic period (ca. 12,000-10,000 B.C.) (13). The Natufian culture (10,300-

8500 B.C.) succeeded the Kebaran in the Levant along the eastern coast of the Mediterranean Sea and utilized lime plaster extensively, primarily for architectural applications such as covering walls and floors. By the Pre-Pottery Neolithic Period (7500-6000 B.C.), as in 'Ain Ghazal in Jordan and Jericho in Palestine, architectural plaster was in wide use, and nonarchitectural uses such as fabricating vessels and ornamental objects were appearing. By 4000 B.C., the Egyptians were using both lime and gypsum plaster as mortar to bind construction blocks together.

Pre-pottery societies in the eastern Mediterranean thus had an extensive plaster technology, even by 6500 B.C. Production of plaster required the heating of either limestone or gypsum. Above 800ºC, limestone ($CaCO_3$) loses carbon dioxide to form lime or quicklime (CaO). Addition of water to lime creates slaked lime, $Ca(OH)_2$, which upon application to a surface reabsorbs carbon dioxide from the atmosphere to revert back to calcium carbonate. At a lower temperature (150-200ºC) gypsum (hydrated $CaSO_4$) loses most of its hydration to form dry plaster of paris, which requires only the addition of water to form the pasty mix that may be applied to a surface and allowed to dry to form hard, rehydrated gypsum. Lime plaster tended to be used in pre-pottery cultures of Anatolia and the Levant (roughly, modern Turkey and the eastern shore of the Mediterranean), whereas gypsum plaster was used in Mesopotamia (the land between the Tigris and Euphrates Rivers, roughly parts of modern Iraq and Syria). Plaster production was very energy intensive, and the energy source was timber for fuel. The loss of such resources in the Levant may have been contributory to the abandonment of settlements after 6500 B.C.

These are real chemical processes, involving manipulation of carbon dioxide and water content to control physical properties. Plaster provided a raw material that could transform pebbles into large stones of a desired size and shape, it could provide a smooth architectural surface, or it could serve as a bonding agent (mortar) between other materials. This technology predated pottery, glass, and metal production. During the period 14,000 to 6500 B.C., the chemical industry of plaster had become a major contributor to the culture of the region that has been called the cradle of Western Civilization, as plants and animals were being domesticated and as hunter gatherers were creating permanent settlements.

Ceramics

At some distant time, very creative humans made the connection between the effects of fire on clay and the accidentally hardened objects that they must have observed in the residues of fires. The first evidence for such activities has been found in Moravia in the Czech Republic (14). The site of Dolni Vestonice near Brno yielded a small (4.5-inch-tall) figurine of a woman with broad hips and pendulous breasts, one of many examples from Central Europe of the so-called Venus figurines from the Gravettian culture, 30,000 to 22,000 years ago. What sets the Venus of Dolni Vestonice apart is that it was made of fired clay, whereas all the other surviving Venuses were carved from stone, ivory, or bone. Moreover, the Moravian site contained two kilns and over 7000 ceramic fragments. These people clearly had discovered that fired clay had special properties, which they exploited entirely for artistic purposes. There is no evidence for utilitarian pieces such as ceramic vessels. The discovery in fact may have been a technological dead end, as no further examples of fired clay occurred for many millennia.

Wet clay possesses the remarkable properties of being able to be shaped (plasticity) and then to hold that shape upon drying (15). The resulting objects, however, are brittle and quickly crumble away. Such objects have rarely survived from antiquity. The third and most remarkable property of clay is its response to heating. Clay is composed of a silicate (Si-O) matrix in which many of the silicon atoms have been replaced by aluminum (hence, aluminosilicate). On heating to above about 600°C, this lattice irreversibly loses molecules of water that were inherent parts of the original structure. The resulting dehydrated structure is permanently hardened. Above about 850°C, further changes occur, called vitrification because of the smoothing effect it has on the material. As the temperature increases, the strength increases and the porosity decreases, making a more useful object. The material is termed earthenware when produced from the range 900-1100°C and stoneware from the range 1200-1300°C. Porcelain requires an even higher temperature, as well as a special type of raw material mix. All these materials are varieties of pottery and examples of ceramics. The latter term further applies to other materials produced by heating, such as bricks, tiles, or small ornamental objects such as the Gravettian Venus.

The discovery of pottery was driven by the utility of the products, which for the most part were vessels to hold solids and liquids. Materials could be stored, cooked, and transported in these vessels. The earliest archaeological records of pottery have been found in Japan, dating back as early as 14,000 B.C. The sites of Kamino and Odai Yamamoto on Honshu and the Fukui and Sempukuji Caves on Kyushu have yielded these extraordinarily early examples of pottery, corresponding to the Incipient Jomon period, or even earlier. Evidence for pottery in China and the Russian Far East was either contemporaneous or followed soon thereafter (if one considers a millennium or two "soon"). Pottery was well established and widespread in Eastern Asia at these early dates. The appearance of pottery in Western Civilization may have been an independent discovery or may have occurred by slow diffusion. It first appears at the sites of Çatalhöyük and Belbidi Cave in Anatolian Turkey, dating to 8500-8000 B.C. Certainly an independent discovery, pottery appeared in the New World during the period 2500-2000 B.C. in Ecuador, Colombia, Mexico, and the southeastern United States.

It should be noted that the raw materials of pottery involve more than clay and water. Substances formed from only these two constituents dry and harden on heating with structural shrinkage and cracking, so that the products are unstable. To circumvent this problem, early potters added a third component to the mix, called a temper or filler. Such a discovery was made throughout the world, with a wide variety of tempers, including sand, limestone, mica, straw, and dung (recall the Biblical bricks without straw). These materials not only enhance stability but also assist the process of vitrification. After the clay, temper, and water are mixed to form a paste, the object is shaped and allowed to dry before firing. Sometimes at this stage it is dipped into a very dilute suspension of the clay in water to provide a thin surface layer, called a slip, which smoothes the surface and creates a background for decoration. Alternatively, the object may be covered with a glaze for surface decoration. This glassy material may be fired at the same time as the clay or applied to the object after firing and then subjected to a second firing. Glazed pottery has been variously called majolica or faience.

Either the slip or the glaze can contain pigments to give color to the surface. The color of the clay itself is determined by several factors, including the specific elements present in the clay, the temperature at which it is fired, and the level of oxygen during firing. Normally the iron content creates reds and blacks. An excess of oxygen in the atmosphere (oxidizing conditions) gives rise to pink, red, or orange colors largely from the pres-

ence of Fe_2O_3. In the absence of oxygen (reducing conditions), blacks and grays occur, from either charred organics or reduced iron (FeO). High levels of calcium, when fired at 1100-1200°C, create a light-colored product termed creamware. At even higher temperatures, the white body of porcelain is formed, given the right kind of clay and temper.

Today the chemist can analyze every component of the pottery—clay, temper, slip, and glaze. The minerals present in the clay often can be determined by X-ray diffraction, the source of the clay by elemental analysis, the type of temper by optical microscopy, and the oxidizing nature of the atmosphere and possibly the firing temperature by Mössbauer spectroscopy. In this way the chemist can recreate the technology that originally gave rise to the product.

Metals and Metallurgy

The earliest worked material that has survived in the archaeological record is stone. Examples go back more than a million years to our predecessor species. The dominant worked material at a given time has given rise to the archaeologist's name for the period, in this case the Stone Age, divided into the Paleolithic (Old Stone Age) and Neolithic (New Stone Age, associated with farming and a settled existence). There may have been a Wood Age that preceded the Stone Age, as wood always was widely available and easily worked, but its instability during burial has left few remains but ashes. Certainly every available type of stone at some time was examined for the utility of its properties. On rare occasions, humans encountered stones that were plastic or malleable. On application of pressure, they altered their shape instead of chipping. These properties have obvious advantages. A damaged tool could be repaired by hammering. Moreover, new shapes could be created, such as flat sheets, which are impossible to achieve by chipping.

These malleable materials were native metals, mostly copper, silver, or gold. They were exceedingly rare and hence did not see widespread utilitarian applications. Copper normally is found in ores as the oxide or sulfide, materials that bear no obvious physical relationship to the native metals. The discovery of the relationship between copper ores and copper metal must be considered one of the most significant in human history (16). It probably occurred either as the result of heat treatment of stones or the use of stones in hearths or pottery kilns. The earliest evidence for the extraction of elemental metal from oxygen or sulfide ores, the process of smelting, has been found at the site of Çatalhöyük in Anatolia (Turkey) during the period 7000-6000 B.C. Although there was increased incidence of copper in the archaeological record at this time, metallurgy was only a peripheral industry for several thousand more years. The problem was that copper metal is relatively soft and hence not so useful for many tools. By the fourth millennium B.C. there was sufficient production of copper to warrant naming the period of the culture the Chalcolithic (Copper Stone) Age, intermediate between the Neolithic and Bronze Ages.

The second major metallurgical discovering was the mixing of metals to form alloys. The presence of a second metal produced a new material that was harder and less brittle than native metal: bronze. The first admixture with copper contained arsenic (arsenical bronze), possibly as the result of the use of arsenic-containing copper ores. Tin emerged as the additive of choice in the Old World during the millennium 4000-3000 B.C., the Early Bronze Age. The full flowering of the Bronze Age in the eastern Mediterranean was 3000-1200 B.C. or so. There has been a longstanding question in archaeology as to the source of tin for the Bronze Age. The ample tin mines of China and South America of course were not available, and the famous mines of Cornwall and Spain were not to be discovered until after 1000 B.C. Recent evidence has indicated that tin was mined in Turkey at the right period of time to help initiate the Bronze Age (17). Ancient peoples experimented with many other alloys, including brass (copper-zinc) especially in India, leaded bronze (copper-tin-lead) favored by the Romans, electrum (gold-silver) in the eastern Mediterranean, and tumbaga (copper-gold-silver) in the New World.

Some time during the second millennium B.C., iron began replacing copper for tools and weapons in the Mediterranean world. The change may have been brought about for a combination of reasons: shortages of the raw materials for bronze, appreciation of the superior properties of iron, or the economic advantage of the wide availability of iron ore raw materials. As with copper ores, iron ores had to be smelted. The Iron Age could not begin until this technology was well worked out. After 1500 B.C., the Hittite people in the Anatolian peninsula were using iron tools and weapons extensively. By 1200 B.C., the traditional transition point between the Bronze and Iron Ages, the Hittites had learned to alloy iron with carbon to produce steel. After 1000 B.C., as the Hittite culture declined, iron technology diffused

westward to the Hallstatt culture of central and western Europe and eventually to Britain by about 500 B.C. Thus the Iron Age began at different times for different places. Possibly independent discoveries of iron technology occurred during the Shang Dynasty in China before 500 B.C. and by the Nok culture in Nigeria by 400 B.C. It was never discovered in the New World.

It is worth noting that the ages of humanity (Stone Age, Copper Age, Bronze Age, and Iron Age) are named after the chemical substances that dominated the technology of the period. Chemistry was helping to define culture.

The archaeological chemist today analyzes metal artifacts to determine the nature of the alloy (18). Trace elements or isotope ratios may indicate the source of the metal ore or the authenticity of the artifact. The profile of trace elements in native copper has been used widely as a means to determine the sources of copper ores on a worldwide basis (19). The ratios of lead isotopes are similarly useful in determining the source of lead. The level of gold impurities in silver coins has been used as a test for authenticity. Modern refined silver is much purer than ancient silver. Thus some coins attributed to the Sassanians (from Iran during the 2nd to the 6th centuries A.D.), have been determined to be modern fakes because they had insufficient levels of gold as an impurity (20). The artificer was unaware that current silver stocks are too pure.

Bread, Beer, and Wine

It has already been argued that chemical technology was applied to food in the form of cooking at a very early stage. The next significant development of food technology was domestication of plants and animals, a biological rather than a chemical process. The baking of bread can be considered a biochemical process, and its roots go back 10,000 years or more in Southwest Asia (21). Baking may even have preceded domestication of grains. Humans would have found that the processing of wild grains could provide a stable, nutritious material through treatment with yeast and heat. Selection of superior strains of grain over many generations then resulted in plant domestication and settled farming.

Like bread, beer is not a naturally occurring food but must be created by human processing. The specific grain barley (*Hordeum vulgare*, from the wild species *H. spontaneum*) was one of the earliest cultivars, along with wheat, and it is the only grain from which true beer can be made. Early beer did not contain hops, but was the direct result of the fermentation of barley. Both bread and beer were staple materials in ancient Mesopotamia and Egypt and probably required the development of pottery before they could achieve widespread use. A rice beer was consumed in China during their Neolithic period, 7000-5000 B.C. (22).

McGovern has tracked the production of wine back into Neolithic times (23). There is clear evidence for wine at the Iranian site of Hajji Firuz Tepe dating to 5400-5000 B.C., and even possibly earlier in transcaucasian Georgia. These studies are carried out by extracting residues from the interior of carefully excavated pots. The molecular marker that identifies exposure of the pot to wine is tartaric acid. Similar experiments for beer use calcium oxalate as the marker. The presence of starch molecules can indicate either bread or beer. Without chemical analysis, the archaeologist would have nothing more than a piece of pottery and no knowledge of its original contents. Thus ancient biochemistry enabled the alteration of natural foods to processed foods, and modern chemistry reveals the presence of these materials in the archaeological record.

Glass

Although sand and quartz are abundant sources of silica (a polymeric form of silicate with the overall formula of SiO_2), its melting point at ca. 1700ºC is far too high to have been achieved by ancient craftsmen. Nonetheless, silica (usually from quartz) is the principal component, or former, of glass. Numerous beads, called Egyptian faience, were produced during the third and fourth millennia B.C., but they involved sintering rather than melting of quartz. Complete melting, however, was required before practical objects such as vessels could be produced. Some time around 2000 B.C. in Egypt or Mesopotamia, it was discovered that the melting point of silica could be lowered significantly by the addition of a second material, or flux. The technology could have emerged from either a pottery or a metallurgy tradition, as both had procedures that could be considered precursors of glass. Around 1500 B.C., glass manufacture suddenly appeared as a major industry in Egypt. The Egyptians, and possibly their Mesopotamian predecessors, used soda ash (sodium carbonate) as the flux from both inorganic sources such as the mineral natron and organic sources such as alkali plants (salcornia). A third component was added as a stabilizer to counter the high solubility of sodium that would destabilize the product. It contained less soluble ions such as calcium or mag-

nesium from sources such as lime. The resulting product for millennia has thus been called soda lime glass. Basically the same formula has been used up to the present in inexpensive window glass.

Most silica sources contain iron ions as an impurity, conveying a light blue-green color to the glass. This color is visible to the eye by viewing a glass pane from its edge. The normal view of glass is through a width of less than an eighth of an inch. Viewing a glass pane from the edge gives a depth of six inches or a foot or more, and suddenly the glass appears to be greenish. The color of the iron ions is manifested by their greater numbers in the greater depth. Ancient chemists realized that adding antimony (which of course they did not know as antimony) to the glass raw material counteracted the coloring properties of iron (which they also did not know as such). The antimony served to oxidize the more colored Fe(II) to the less colored Fe(III), decreasing the coloring. High antimony glass was in use from the sixth century B.C. to the fourth century A.D. Chemical analysis of glass for antimony thus can indicate the general period of production. In Roman glass, manganese replaced antimony as the decolorant. Wherever Roman influence was uppermost, the level of antimony decreased and that of manganese increased, another chemical fingerprint for glass technology.

Mediterranean glass technology developed in many directions. Various elements could make it colored: deep green from copper, red from copper in a different oxidation state, violet from iron and manganese, blue from cobalt, turquoise blue from copper and iron, and yellow from lead and antimony, usually at levels under 1% as the oxide. Normally such glass was transparent, but the addition of sufficient lead (giving a yellow color), antimony, or tin (giving a white color) made the glass opaque. The Egyptians learned how to bond glass to metal, resulting in the technology of enameling. A Hellenistic innovation was layered or cased glass, by which several glass layers were placed one on top of the next, and designs were cut through to different layers, creating cameos. Dichroic glass, which exhibits one color to reflected light and a different color to transmitted light, appeared in the late Roman Empire. The Lycurgus Cup, dated to the fourth century A.D., contains nanometer-sized particles of gold and silver, whose dimensions are appropriate to reflect or transmit light of different wave lengths. Nanotechnology also was known to the Chinese, who employed nanodimensional gold particles to produce brilliant red colors of the porcelains termed *famille rose*.

Sayre and Smith first recognized the importance of bulk elemental composition on the properties of glass (24). The roles of sodium as a flux and of antimony or manganese as a decolorant have been mentioned. Lead was used as an alternative to sodium as the flux in Mesopotamia and China and as a means to enhance the brightness of the glass by the Romans and later by Islamic and European cultures. Early Chinese glass contained barium as well as lead as the flux, but the more stable soda glass, introduced by diffusion from the West, replaced the earlier formulation after the Eastern Han Dynasty (220 A.D.). After the fall of the Roman Empire, sources of soda become unavailable to glass manufacturers in Europe away from the Mediterranean coast. Plant ash rich in potassium was used as the flux instead. As a result, medieval glass from much of Europe was high in potassium.

The elemental composition of glass provides an amazing witness of the ebb and flow of economic, environmental, and social pressures. Antimony was a better decolorant than manganese, but the Romans preferred the latter, probably because of its availability. China developed lead and barium fluxes independently of Western discoveries but quickly adopted the superior soda formulation when it become known to them. Medieval Europe moved away from soda glass in favor of potash glass for reasons of availability. Lead was found to clarify glass to a point of sheer brilliancy. Small particles of gold could deliver very unusual appearances. Almost any color could be achieved with the right additives. These discoveries must have been the result of careful observations and luck, just like most of science.

Rubber

Technological developments in the Western Hemisphere generally occurred much later than those in the Old World. Thus pottery did not appear until about 2500 B.C. and metallurgy some time before 250 B.C. The chemists of the New World, although working later in time, were no less innovative than those of Southwest and East Asia. For example, they created a blue pigment used on wall murals that was a combination of the vegetable dye indigo and a specific white clay called attapulgite, making what today would be called an organic-inorganic hybrid. This material has proved to be very stable to acid, base, solvents, light, normal heat, and biological corrosion, allowing the mural colors in Bonampak, Chiapas, to remain bright for hundreds of years in the jungle.

In addition, Mesoamerican chemists created processed rubber about 4000 years ago. It was an easy step to recognize the useful properties of the sticky exudate of the tree *Castilla elastica*. The polymer is polyisoprene, identical to modern crude rubber from the South American plant *Hevea brasiliensis*. This latter species is preferred today because it can yield its exudate without killing the plant. *Castilla elastica* was widely available in Mesoamerica. When dry, however, the unprocessed exudate becomes brittle and loses its rubbery properties. Observations by Spaniards at the time of the Conquest indicated that the local chemists mixed the crude exudate with the juice from the morning glory vine, *Ipomoea alba*. A recent study of the nuclear magnetic resonance (NMR) spectra of ancient Mesoamerican rubber indicated that it is identical to modern processed rubber (25). It differed from the NMR spectra of the crude latex in the absence of proteinaceous resonances. The morning glory juice served not only to purify the exudate but also to generate cross linking, analogous to the modern process of vulcanization. The purified, cross-linked material retains its elastic properties.

The Mesoamericans used rubber primarily to make the ball for the religious activity termed *pelote*, now referred to as a ball game. *Pelote* courts are found at archaeological sites from the southwestern U.S. to Central America, indicating an extremely widespread activity, which has been associated with agricultural fertility. In addition, rubber was occasionally used for bands to hold implements to handles and for decoration. These artifacts have been excavated particularly from the *cenotes* or water-filled sinkholes in Yucatan. Without chemical processing, the rich ceremonial culture of the *pelote* game would never have developed. Western civilization did not have vulcanized rubber until the nineteenth century.

Overview

Hundreds of thousands of years ago, hominids from a species ancestral to *Homo sapiens* became chemists by learning how to control fire. This control provided heat, light, and protection, aiding hominids to expand throughout this tenuous and dangerous world. Fire later provided the means to process food, through cooking, into more stable, safer materials and to process flint and other stones, through annealing, into more useful materials. By mixing minerals with natural tars, humans created a new material (asphalt) with superior properties for adhesive purposes. Fire also enabled humans to convert

limestone and gypsum into a powder. Addition of water formed a slurry, which could be formed into structures and allowed to harden into shaped stone. All these chemical processes were in use more than 10,000 years ago.

Chemistry and biology worked together to give rise to the Neolithic revolution, as hunters and gatherers became farmers and began to congregate in villages. Chemistry's first profound contribution to this revolution was pottery, which appeared in Japan about 14,000 B.C., Turkey 8500 B.C., and the New World 2500 B.C., all most likely independent discoveries. Ceramic figurines existed much earlier, but the invention of utilitarian ceramic vessels provided rich uses in early Neolithic cultures. The earliest system of writing, cuneiform, invented by the Sumerians about 3200-3000 B.C., was executed on baked clay. Thus chemistry provided a key element in the development of that most basic characteristic of civilization, writing. The Sumerians appreciated how momentous their invention was and celebrated it in one of their later epics:

> Before that time writing on clay had not yet existed,
> But now, as the sun rose, so it was! The king of
> Kullaba had set words on a tablet, so it was!

Kullaba was ancient Uruk (the exclamation points have been provided by modern editors).

With the availability of ceramic vessels, processed food could be stored and manipulated. Grain was converted to bread and beer, grapes to wine. The baking of bread was carried out by 8000 B.C. In fact, the sequence of events is not clear, as to whether grain domestication (a biological process) or baking of bread (a biochemical process) came first. The invention of beer provided a staple drink that may have been safer and more nutritious than water sources subject to microbial contamination (many microorganisms cannot exist in the presence of ethanol).

Humans moved from the Stone Age (which includes the Neolithic) to the various ages of metals (Chalcolithic, Bronze, Iron) by means of a series of chemical discoveries. The mixing of elemental materials into alloys improved the properties of copper (as bronze) and of iron (as steel). The smelting of ores allowed natural oxides and sulfides to be converted to the elemental form needed for metallic materials. Stone tools and weapons were replaced with metallic ones.

The invention of glass was made possible by the chemical discovery that a mixture of sand with soda

could be liquefied and converted to useful objects on solidification. Less revolutionary than metals (the times were referred to as the Bronze Age, not the Glass Age), glass nonetheless allowed both utilitarian objects and materials appreciated just for their beauty to be created on a scale heretofore unknown.

All these chemical discoveries, except possibly glass, were made by preliterate societies; yet they helped define human culture wherever it was found.

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