# Symposium on Chemistry & Culture

43<sup>rd</sup> IUPAC World Chemistry Congress San Juan, Puerto Rico

Monday, August 1, 2011





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# Protochemistries are the Bridge

Roald Hoffmann

### Protochemistries

Transformations of matter accomplished before there were professional chemists

### Protochemistries

Transformations of matter accomplished before there were professional chemists

winning metals from their ores

cooking, preserving food, fermentation, distillation

medicines

ceramics, glass, and other container materials

dyes, textile preparation

cosmetics

jewelry

pigments

tanning

soap, other cleaning agents

mummification



Heather Lechtman





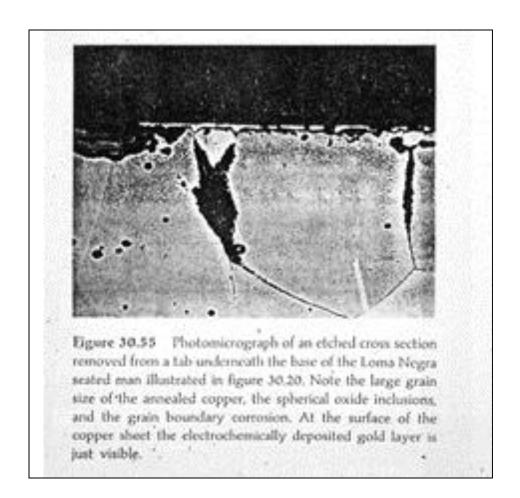


Moche, Chimu, Inca









Heather Lechtman

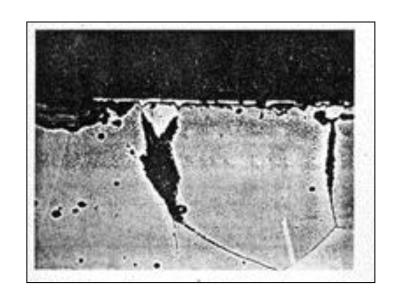
### Aqua regia = $HCI + HNO_3$ 3 volumes to 1

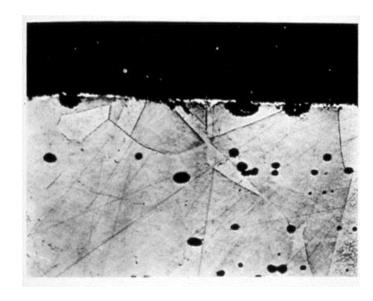
AuCl<sub>4</sub>-

### Aqua regia = $HCI + HNO_3$ 3 volumes to 1

AuCl<sub>4</sub>-

Chile saltpeter + salt + alum  $NaNO_3 + NaCl + KAl(SO_4)_2.12H_2O$ 



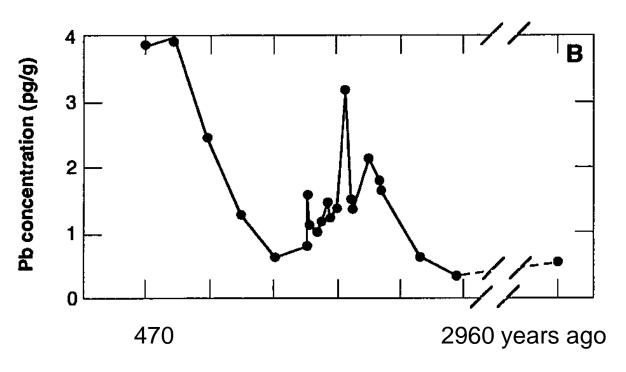


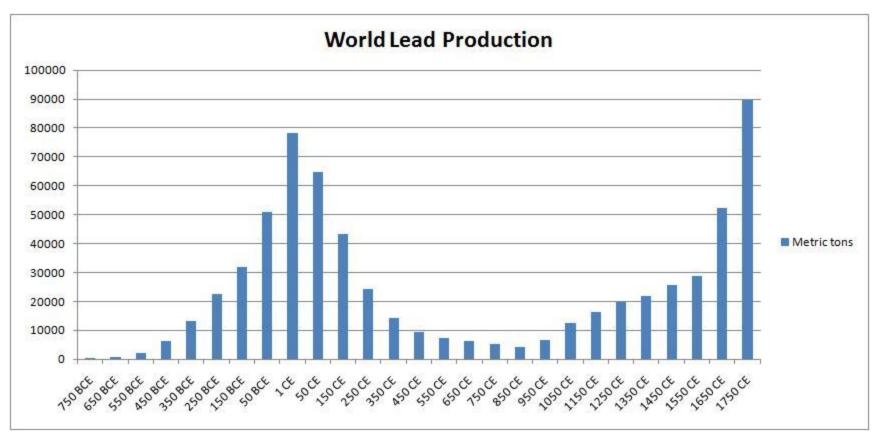
## Greenland Ice Evidence of Hemispheric Lead Pollution Two Millennia Ago by Greek and Roman Civilizations

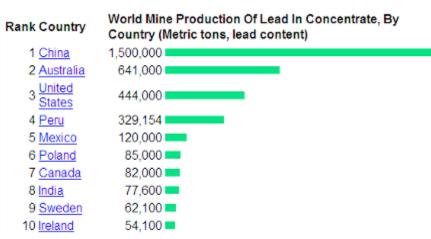
Sungmin Hong, Jean-Pierre Candelone, Clair C. Patterson, Claude F. Boutron\*

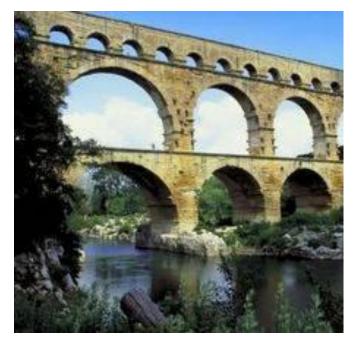
Science, 265, 1841 (1994)















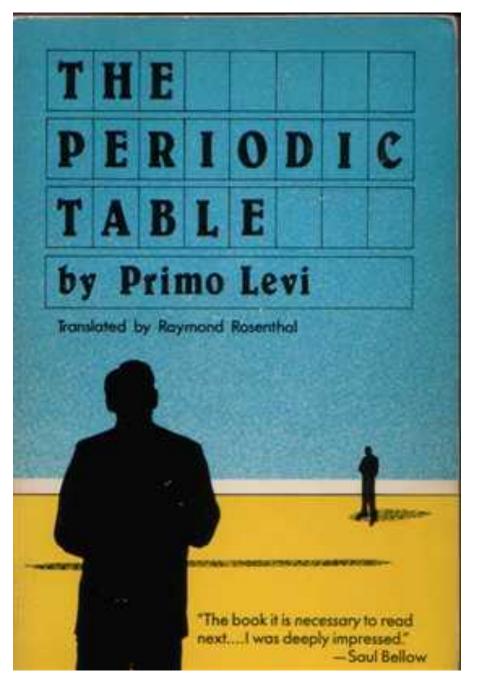


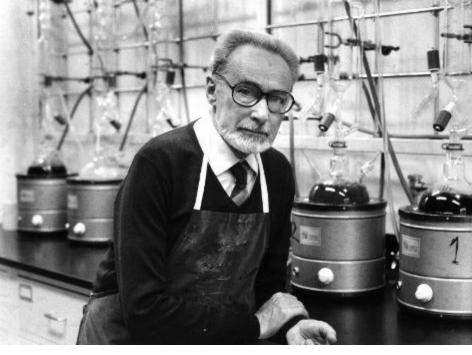
# Greenland Ice Evidence of Hemispheric Lead Pollution Two Millennia Ago by Greek and Roman Civilizations

Sungmin Hong, Jean-Pierre Candelone, Clair C. Patterson, Claude F. Boutron\*

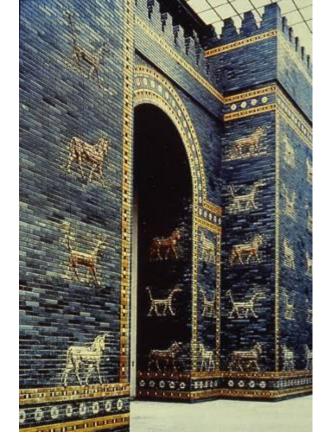
Analysis of the Greenland ice core covering the period from 3000 to 500 years ago—the Greek, Roman, Medieval and Renaissance times—shows that lead is present at concentrations four times as great as natural values from about 2500 to 1700 years ago (500 B.C. to 300 A.D.). These results show that Greek and Roman lead and silver mining and smelting activities polluted the middle troposphere of the Northern Hemisphere on a hemispheric scale two millennia ago, long before the Industrial Revolution. Cumulative lead fallout to the Greenland Ice Sheet during these eight centuries was as high as 15 percent of that caused by the massive use of lead alkyl additives in gasoline since the 1930s. Pronounced lead pollution is also observed during Medieval and Renaissance times.

Science, 265, 1841 (1994)







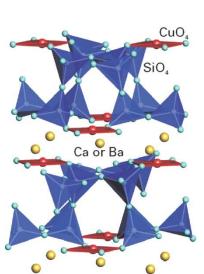




Lapis lazuli = ultramarine









Tyrian purple

24If this was done unwittingly, through the inadvertence of the of the with its

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30But the person, be he citizen or stranger, who acts defiantly4 reviles the LORD; that person shall be cut off from among his people. 31 Because he has spurned the word of the LORD and violated His commandment, that person shall be cut off-he bears his guilt.

<sup>32</sup>Once, when the Israelites were in the wilderness, they came upon a man gathering wood on the sabbath day. 3) Those who found him as he was gathering wood brought him before Moses, Aaron, and the whole community. 34He was placed in custody, for it had not been specified what should be done to him. 35 Then the LORD said to Moses, "The man shall be put to death: the whole community shall pelt him with stones outside the camp." 36So the whole community took him outside the camp and stoned him to death-as the LORD had commanded Moses.

37The LORD said to Moses as follows: 38Speak to the Israelite people and instruct them to make for themselves fringes on the

corners of their garments throughout the ages; let them attach a cord of blue to the fringe at each corner. 39 That shall be your fringe; look at it and recall all the commandments of the LORD and observe them, so that you do not follow your heart and eyes in your lustful urge. 40 Thus you shall be reminded to observe all My commandments and to be holy to your God, 41I the LORD am your God, who brought you out of the land of Egypt to be your God: I, the LORD your God.

סרח

16 Now Korah, son of Izhar son of Kohath son of Levi, "betook himself, a along with Dathan and Abiram sons of Eliab, a and On son of Peleth-descendants of Reuben+2to rise up against Moses, together with two hundred and fifty Israelites, chieftains of the community, chosen in the assembly, men of repute, <sup>3</sup>They combined against Moses and Aaron and said to them, "You have gone too far! For all the community are holy, all of them, and the LORD is in their midst. Why then do you raise yourselves above the LORD's congregation?"

4When Moses heard this, he fell on his face. 5 Then he spoke to Korah and all his company, stying, "Come morning, the LORD will make known who is His ard who is holy, and will grant him access to Himself; He will grant access to the one He has chosen. 6Do this: You, Korah and all your4 band, take fire pans, 7and tomorrow put fire in them and lay incense on them before the LORD. Then the man whom the LORD chooses, he shall be the

holy one. You have gone too far, sons of Levi!"

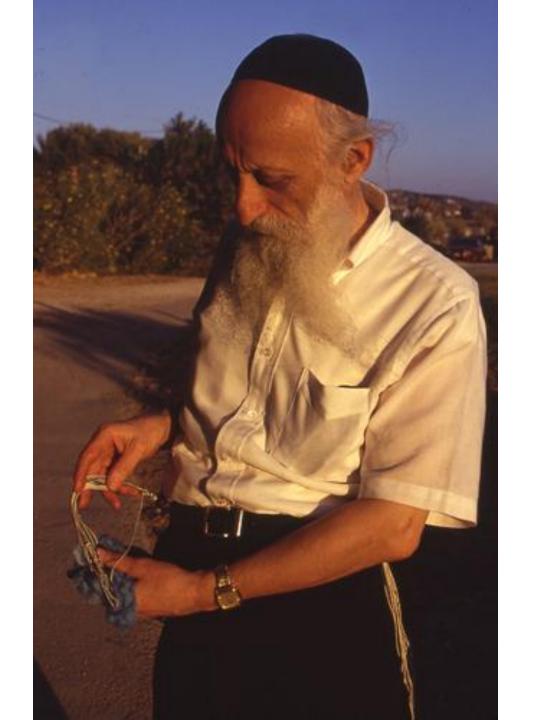
Moses said further to Korah, "Hear me, sons of Levi. Is it not enough for you that the God of Israel has set you apart from the community of Israel and given you access to Him, to perform the duties of the LORD's Tabernacle and to minister to the community and serve them? 10 Thus He has advanced you and all your fellow Levites with you; yet you seek the priesthood too! 11 Truly, it is against the LORD that you and all your company have banded together. For who is Aaron that you should rail against him?"

4 Lit. "his"

wa Lit, "took"; Heb obscure

bb According to Nu. 26.5, 8-9, Eliob unt ton of Pullu, ton of Reuben

Perhaps in the sense of "his face fell"

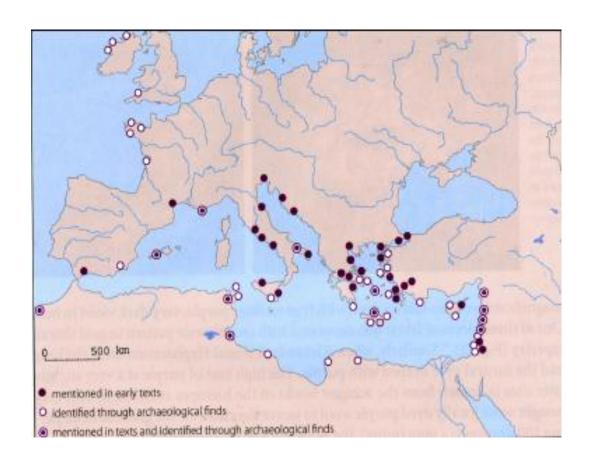




















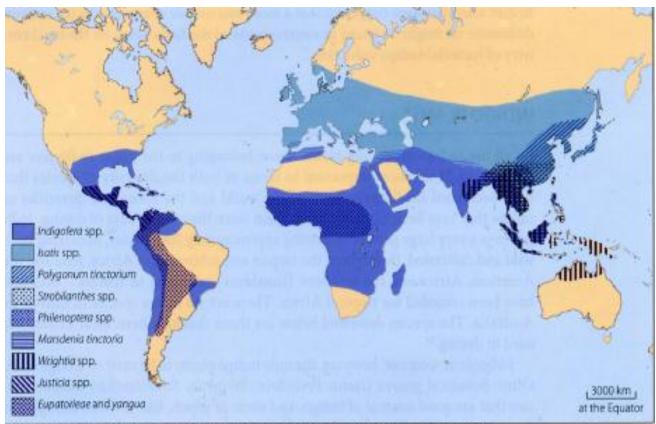


Figure 25 Indigo plants of the world and American blue vat dyes. (Map: D. Augerd/ D. Cardon, CNRS)



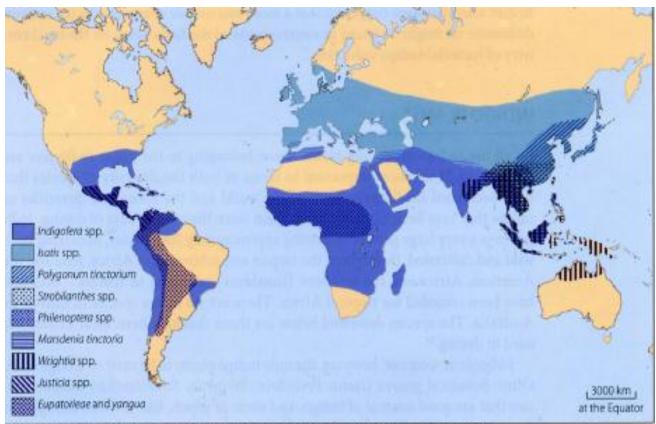
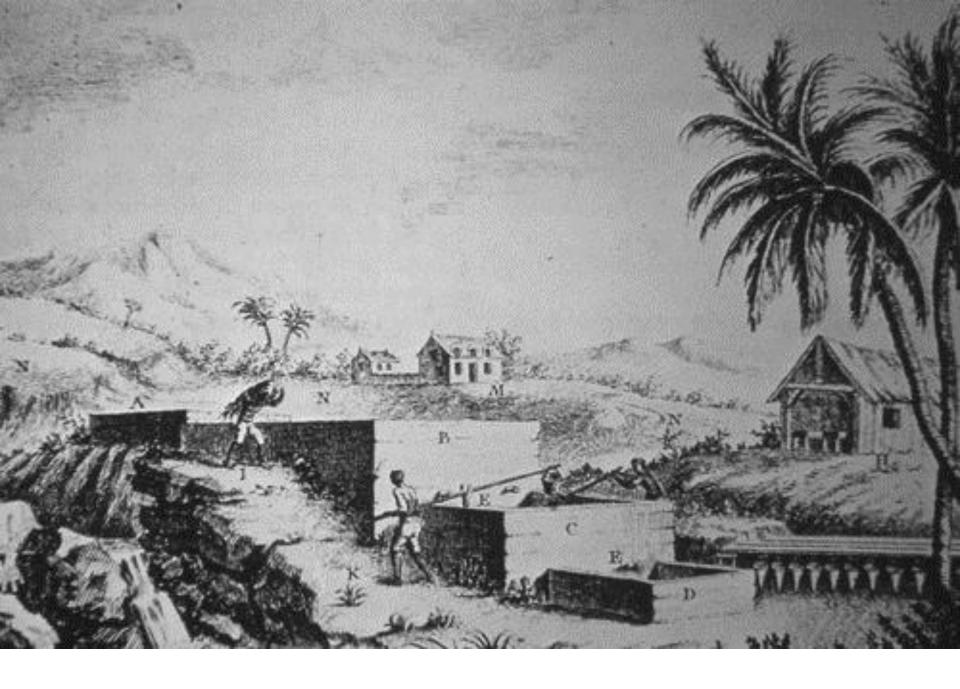


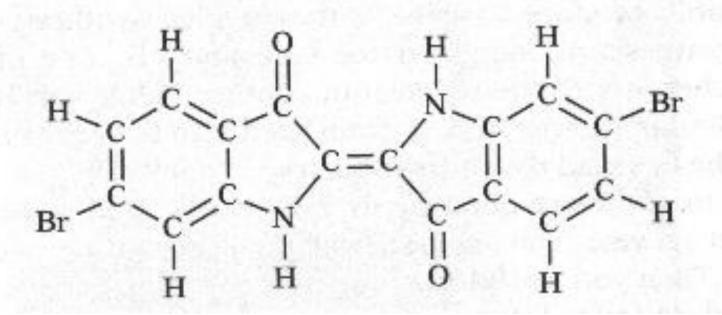
Figure 25 Indigo plants of the world and American blue vat dyes. (Map: D. Augerd/ D. Cardon, CNRS)





Diderot et D'Alembert

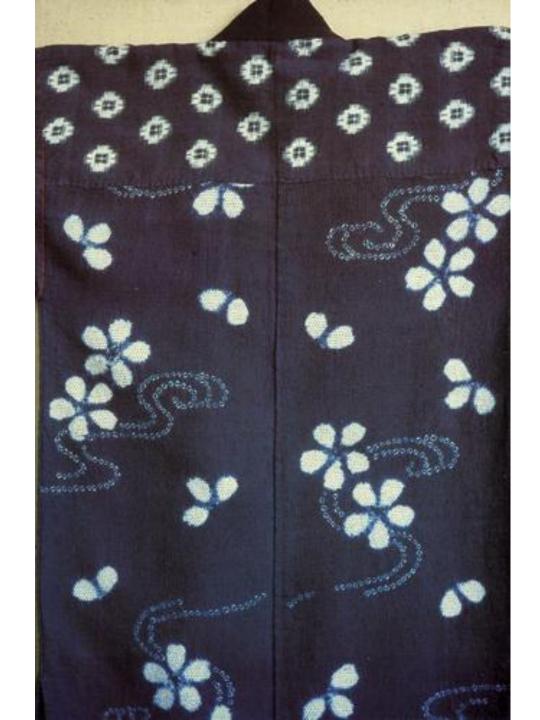




### Historic Dye Labels of BASF Indigo since 1890







### 105. Dyeing in Dark Blue.

Put about a talent of woad in a tube, which stands in the sun and contains not less than 15 metretes, and pack it in well. Then pour urine in until the liquid rises over the woad and let it be warmed by the sun, but on the following day get the woad ready in a way so that you (can) tread around in it in the sun until it becomes well moistened. One must do this, however for 3 days together.

Stockholm Papyrus

# Accounts Chem. Res. 1990, 23, 152-8 Royal Purple Dye: The Chemical Reconstruction of the Ancient Mediterranean Industry

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Museum Applied Science Center for Archaeology, University Museum, University of Pennsylvania, Philadelphia, Pennsylvania 19104
Received December 6, 1989 (Revised Manuscript Received February 2, 1990)

Royal purple, 6,6'-dibromoindigotin (DBI, structure III in Figure 1, X = Br), is the most renowned of ancient dyes.<sup>1</sup> Even before Nero issued a decree in the first century A.D. that gave the emperor the exclusive right

Patrick E. McGovern was born in Corpus Christi, TX, in 1944. His academic background combined the physical sciences, archaeology, and history: an A.B. in Chemistry from Cornell University and a Ph.D. in Near Eastern Archaeology and Literature from the Oriental Studies Department of the University of Pennsylvania. Since 1979, he has been a Research Scientist in the Museum Applied Science Center for Archaeology (MASCA), where he has been engaged in a wide range of research in archaeological chemistry, including radiocarbon dating, cesium magnetometer surveying, colorant analysis of ancient glasses, pottery technology, and organic analysis of vessel contents and dives.

Rudolph H. Michel was born in Landau, Germany, in 1925 and came to the U.S. in 1936. He was trained as a physical organic chemist, receiving his B.S. from the City College of New York and his Ph.D. from the University of Notre Dame. He investigated various aspects of polymer chemistry, including the syntheses of many new materials, in his professional career at E. I. du Port de Nemours & Co., from which he retired as a Research Fellow in 1985. Soon afterward and continuing to the present, he volunteered his considerable chemical expertise to begin a new "career" in archaeochemical research at MASCA.

to wear royal purple garments, the association of this dye with royalty and high ecclesiastics was well established. As one example, biblical texts<sup>2</sup> incorporating Iron Age traditions prescribed that the tabernacle curtains and the high priest's vestments were to be dyed with royal purple.

The sociopolitical and religious significance of royal purple was closely tied to its economic value. In some periods, it was worth as much as 10-20 times its weight in gold.<sup>3</sup> This circumstance can be traced to the fact that the precursors of DBI, which convert to the dye in air and light (see Figure 1), are found in nature only in the hypobranchial secretions of certain marine mollusks (Figure 2).<sup>4</sup> As many as 10 000 animals are

 Brunello, F. The Art of Dyeing in the History of Mankind; Neri Pozza Editore: Venice, 1973; pp 13, 57, 79.

(2) See: Exod. 26:1, 31: 28:4-6: 39:1, 28-29. 1 Kings 5:1-12: 7:13-14:
 9:10-14, 26-28; 10:11, 22. 2 Chron. 2:7, 14; 3:14. Ezek. 27:7, 16: 24.
 (3) Born, W. Ciba Rev. 1937, 1, 106-111, 124-128.

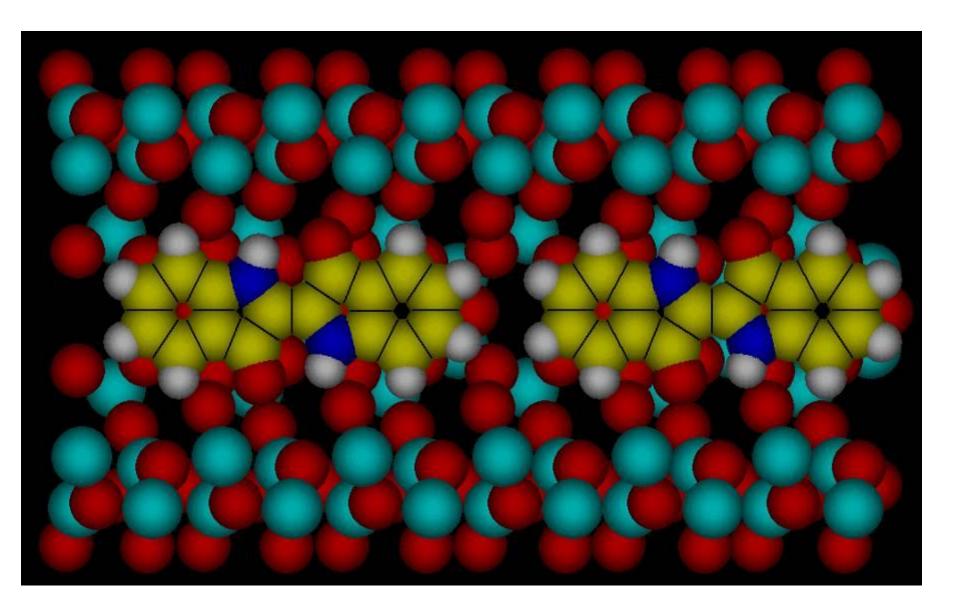




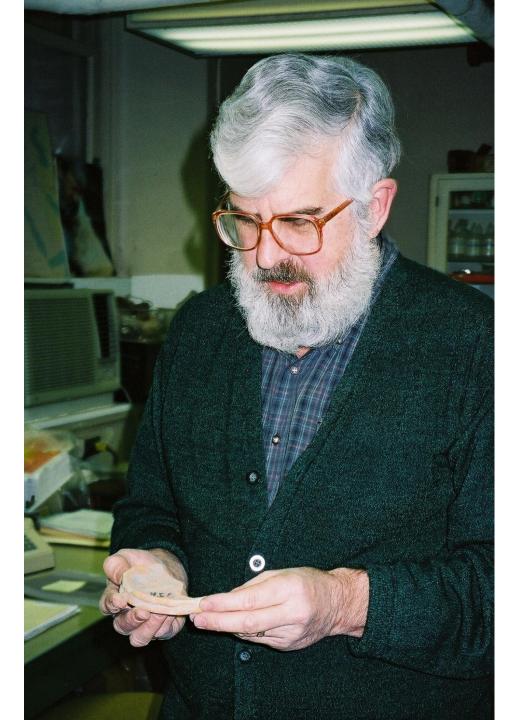












Patrick McGovern

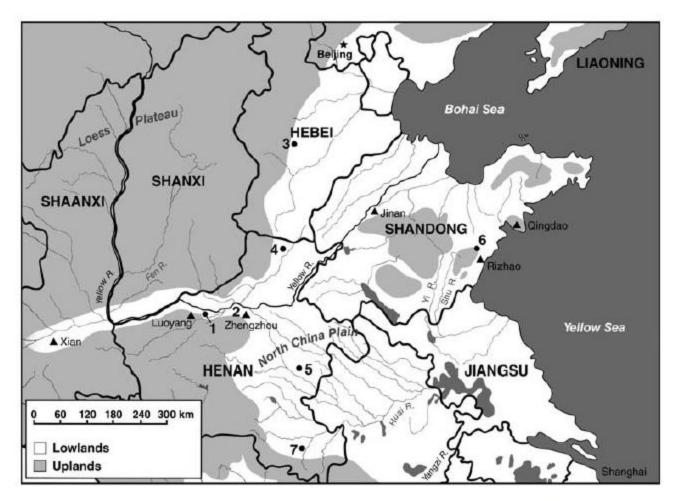
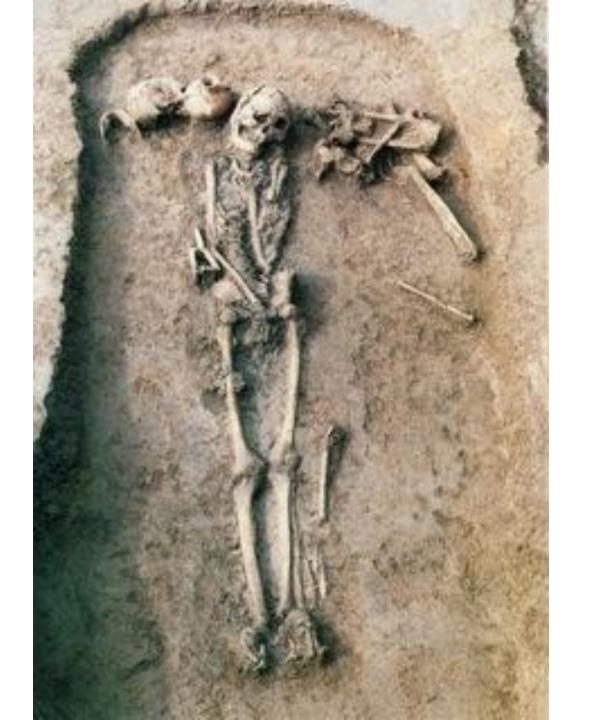


Fig. 1. Archaeological sites discussed in the text. 1 = Erlitou, 2 = Zhengzhou, 3 = Taixi, 4 = Anyang, 5 = Jiahu, 6 = Liangchengzhen, 7 = Tianhu.



~7000 BC



# Chemical Identification and Cultural Implications of a Mixed Fermented Beverage from Late Prehistoric China



PATRICK E. McGOVERN, ANNE P. UNDERHILL, HUI FANG, FENGSHI LUAN, GRETCHEN R. HALL, HAIGUANG YU, CHEN-SHAN WANG, FENGSHU CAI, ZHIJUN ZHAO, AND GARY M. FEINMAN

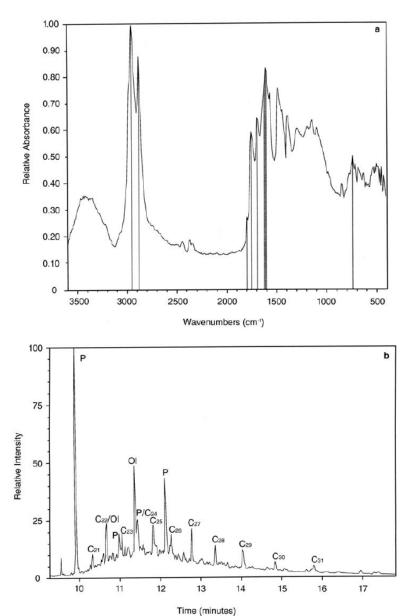


Fig. 5. Representative chemical results for Liangchengzhen mixed fermented beverage. a = DRIFTS spectrum of sample no. 1 (methanol extract), a tongxing bei tubular cup, showing the principal absorptions of the mixed fermented beverage of rice, honey, and fruit. Spectra deresolved at 8 cm<sup>-1</sup> wavenumber. See text for discussion. b = GC/MS analysis of sample no. 2 (chloroform extract), total ion chromatogram, a gaobing bei tall-stemmed cup, showing the homologous parafin series from  $C_{21}$  to  $C_{31}$  (P = phthlate contaminant; Ol = oleamide contaminant). Chinese beeswax has elevated levels of the odd-numbered members of the series.

#### A MIXED FERMENTED BEVERAGE

The combined chemical results for the large group of twenty-three Liangchengzhen samples are best explained as a mixed fermented beverage composed of rice, honey, and a fruit, possibly with barley and a plant resin (or herb) as additives (listed in the last column of Table 1). A beverage in which rice was a principal ingredient accords with archaeobotanical findings thus far. Millet, which is also well represented at Liangchengzhen, does not appear to have been used in making the beverage, although barley—yet to be identified archaeobotanically—is suggested by the chemical evidence. At present, although it is not clear when barley was introduced into China or domesticated there, an early date is implied by the finding of archaeobotanical samples as early as ca. 1000 B.C. in Japan and Korea, across the Yellow Sea from Shandong province (Crawford 1992:21–22).

You could call this extreme beverage a "Neolithic grog." It was comprised of honey mead and a combined "beer" or "wine" made from rice, grapes, and hawthorn fruit. Rice is a grain, like wheat and barley, so by that definition it makes a beer (of about 4-5% alcohol), but when it's fermented to 9-10% and has pronounced aromatic qualities, then it's more like a wine. Maybe, the best modern comparison is with an aged Belgian ale or a barley wine.

Although some ingredients have been interchanged, it's also not all that different from Midas Touch in combining a wine, beer and mead, even if Jiahu precedes Midas by some 6000 years.





## Protochemistries are the Bridge

stress the essential importance of <u>experiment</u>, and... of the underlying economics that governs much human activity

render homage to the past, to the ingenuity of human beings

connect our world, in time and in substance

these stories <u>normalize</u> science

and put it in the context of world culture – chemistry in culture, culture in chemistry

### Good Stories in Teaching Chemistry

Storytelling is human, it is old

The facts are... mute. Narrative is tremendously important in science, but it is not recognized as such because it is not "mathematicizable." In this it shares the fate of other human tools for shaping understanding, such as metaphor

After simplicity, I believe storytelling is the main pleasure-giving principle in science

Dignifications of storytelling that scientists do allow themselves: pattern recognition, hypothesis formation