

rona discharge in moist air (the absence of the 1400 cm^{-1} doublet in the spectrum of the products of an $\text{O}_2 + \text{H}_2\text{O}$ corona discharge would suggest this, however).

As a further check, the Raman spectrum of some of the material collected in the moist air discharge was obtained. The transverse excitation geometry described by Pez (13) was used to excite a $0.1\text{-}\mu\text{l}$ sample of the product of the moist air discharge contained in a 0.3-mm quartz capillary by $6328\text{-}\text{\AA}$ He-Ne laser light. The Raman spectrum (Fig. 2A) shows only a single polarized Raman line at 1050 cm^{-1} . Comparison with the Raman spectrum of a 35 per-

cent nitric acid solution obtained under the same conditions (Fig. 2B) strongly supports the identification suggested by the infrared absorption measurements. The Raman spectrum of polywater obtained by Lippincott *et al.* is shown in Fig. 2D. Unfortunately, the polarization conditions were not specified by the authors nor did they report a Raman spectrum for a polywater sample removed from a fine-bore quartz capillary. To the extent that the present conditions duplicate those used by Lippincott *et al.*, the Raman spectrum can be considered to offer a more unique characterization of polywater than the infrared spectrum does.

It can be concluded that the principal product of a positive corona discharge in moist air that was detected in our experiments was a water solution of nitric acid. There are, however, striking similarities between the infrared spectra for nitric acid and those for polywater, particularly in the easily accessible mid-range. Investigators of the polywater phenomenon should thus be very cautious in their use of infrared spectra as a sole means of identification, especially if the polywater samples contain some water. The possibility also exists that nitric acid might be produced in capillaries by the same procedure as that used in the production of polywater and that the nitric acid might be confused with an aqueous solution of poly-

water. Under favorable conditions an air discharge producing nitrogen oxides could occur in the capillary as a result of the charge imbalance created during the drawing process. Subsequent exposure of the capillaries to a moist atmosphere might then allow dissolution of the nitrogen oxides formed to produce nitric acid.

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References and Notes

1. E. R. Lippincott, R. R. Stromberg, W. H. Grant, G. L. Cessac, *Science* **164**, 1482 (1969).
2. For a summary and review of the work, see B. V. Deryagin and N. V. Churayev, *Priroda* No. 4 (Russian) (1968), pp. 16-22.
3. M. M. Shahin, *J. Chem. Phys.* **45**, 2600 (1966); *ibid.* **47**, 4392 (1967).
4. J. M. Williams and S. W. Peterson, *J. Amer. Chem. Soc.* **91**, 776 (1969); J. M. Williams, *Inorg. Nucl. Chem. Lett.* **3**, 297 (1967).
5. J. Lear, *Saturday Rev.* (6 Sept. 1969), p. 50.
6. T. F. Page, Jr., R. J. Jakobsen, E. R. Lippincott, *Science* **167**, 51 (1970).
7. H. Cavendish, *Phil. Trans. Roy. Soc. London* **74**, 119 (1784).
8. T. A. Ford and M. Falk, *Can. J. Chem.* **46**, 3579 (1968).
9. R. A. Marcus and J. M. Fresco, *J. Chem. Phys.* **27**, 564 (1957).
10. M. K. Wilson and R. M. Badger, *ibid.* **16**, 741 (1948).
11. M. Falk and P. A. Giguere, *Can. J. Chem.* **35**, 1195 (1957).
12. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1963), pp. 107-110.
13. Work done by G. Pez, McMaster University, is described by S. K. Freeman and D. O. Landon, in *Spex Speaker* **8**, No. 4 (Dec. 1968) (Spex Industries, Inc., Metuchen, N.J.).
- 14 November 1969; revised 29 January 1970 ■

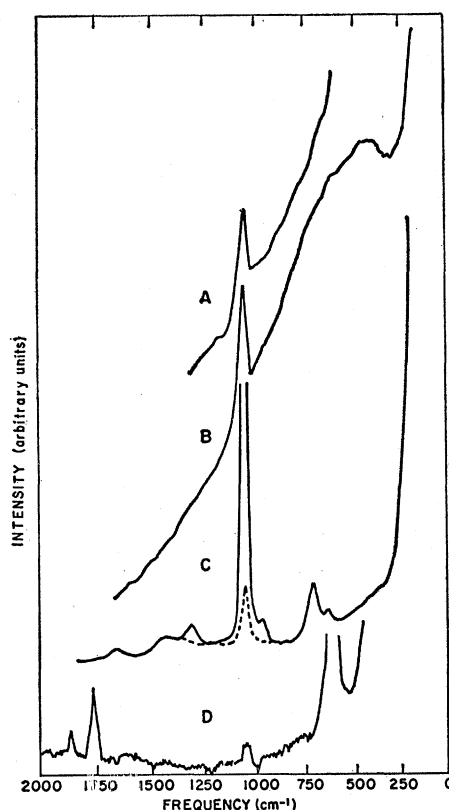


Fig. 2. (A) Stokes region Raman spectrum of products of corona discharge in moist air (incident radiation electric vector polarized perpendicular to the direction of observation of scattered light; the 1050-cm^{-1} line does not appear for parallel polarization). (B) Stokes region Raman spectrum of a 35 percent nitric acid solution in a capillary 0.3 mm in diameter (same polarization condition as those for (A)). (C) Stokes region Raman spectrum of a bulk sample of 35 percent nitric acid solution. Incident radiation electric vector polarized perpendicular to the direction of observation of scattered light (solid line); parallel polarization (dashed line); (the 1050-cm^{-1} line appears weakly for parallel polarization orientation because of the optical geometry required for a bulk sample). (D) Raman spectrum of polywater reported by Lippincott *et al.* (1).

Tumbaga Object from the Early Classic Period, Found at Altun Ha, British Honduras (Belize)

Abstract. Excavations at Altun Ha, British Honduras (Belize), have yielded a claw-shaped bead of tumbaga, a gold-copper alloy, occurring as part of an Early Classic offering. Stratigraphic evidence plus radiocarbon dates place the cache at or before A.D. 500, and stylistic elements indicate a source for the bead in the Coclé culture of central Panama.

Excavations begun in 1964 by the Royal Ontario Museum, Toronto, Canada, at the ancient Maya site of Altun Ha in northern British Honduras (Belize) have demonstrated the existence of a long and complex occupation that extended from at least late Pre-Classic times (about 200 B.C.) to the end of the Classic period (about A.D. 925), with subsequent low-level continued use, or possibly intermittent reoccupation, until the 14th century A.D. The site lies approximately 48 km north of Belize City and 10 km from the Caribbean shore. Its size is

only moderate; the core is about 1 km^2 , and surrounding areas total about 5 km^2 .

The site is marked, however, by considerable architectural richness and unexpectedly great material wealth. Progress reports and summaries of the excavations (1) present data on portions of the site's material culture and architectural history, both of which provide the basis for recognition of long-term, extensive trade relationships between the people of Altun Ha and those of inland and southern portions of the Maya area, as well as central Mexico

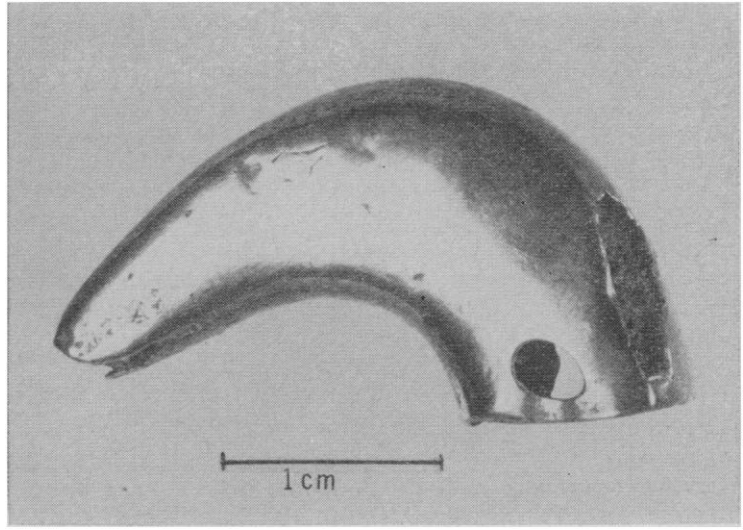
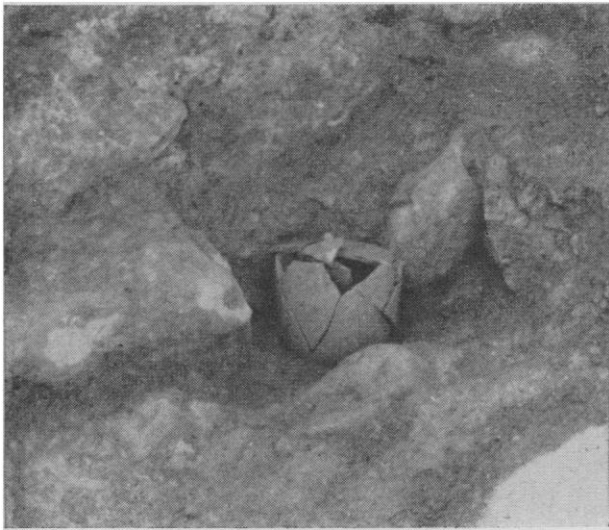


Fig. 1 (left). Limestone offering vessel *in situ*.

Fig. 2 (right). The tumbaga bead. Note corrosion at base, tip, and edges of faces.

and probably the countries of Central America.

Among other results of the 1969 excavations, trenching of a temple that forms part of the southern boundary of the earlier of two plazas in the central ceremonial precinct revealed an unusual offering in the final addition to the building: an undecorated lidded limestone vessel (Fig. 1) containing a variety of jadeite objects, two pearls, laminae of crystalline hematite, six beads of *Spondylus* shell (probably *S. calcifer* Carpenter, a Pacific species), and, most importantly, a single bead of the gold-copper alloy commonly termed tumbaga. Radiocarbon date determinations undertaken by Geochron Laboratories Inc. (samples GX-1641 and GX-1674) indicate that the first major reconstruction of the temple took place between A.D. 125 and 200, and, on the basis of stratigraphy, the final addition to the structure can be dated at no later than A.D. 550. A ^{14}C analysis of the *Spondylus* beads from the offering (sample GX-1689) yielded a date of A.D. 260 ± 120 , with the application of Pacific marine shell corrections. If the necessary lapse in time between collection of the shells and deposition of the beads plus the possibility that the shells were collected some time after the deaths of the organisms are taken into account, the indicated date fits the stratigraphic evidence reasonably well and certainly confirms the physical indications of contemporaneity of the offering and its context. A date somewhat before A.D. 500 is perhaps most probable.

Prior to the discovery at Altun Ha, it was generally believed that gold was

not present in the central Maya area in Classic times. The only possible Classic occurrence of the metal in the entire Maya region was a seemingly questionable inclusion in a sub-stela cache at Copan, Honduras, consisting of the legs of a small hollow figurine, dated at A.D. 782 and probably of Panamanian origin (2). The absence of gold artifacts in Classic Maya sites, a marked contrast with the rich but rather insecurely dated metallurgical traditions of southern Central America, has been attributed in part to the supposed lack of naturally occurring gold in the region; however, a recent geological survey has revealed that small quantities of easily recoverable placer gold, including both fine powder and very small nuggets, are found in the streams of the upland zone of western British Honduras (Belize). The ancient Maya were closely attuned to their environment, and thus their failure to collect gold is likely to have been due to cultural factors, among which the most important was probably lack of metallurgical techniques, although there is some evidence for smelting and casting of copper in the central lowlands in Classic times (3). The color yellow was associated with dying plant life and crop failure in Maya belief, and this unfavorable aspect may also have played a part in the Classic Maya lack of interest in gold as a material for ceremonial use. In any case, it is clear that the tumbaga bead was not manufactured at Altun Ha or elsewhere in the Maya area, and hence its presence in the offering points to trade ties linking the people of Altun Ha with some non-Maya group.

The Altun Ha bead, apparently meant to represent an animal (jaguar?) claw, is formed of thin sheeting, which was probably hammered and annealed, although casting cannot be ruled out. There is a square opening at the base, from which the body tapers along the curve of the object to a slightly rounded tip. Overall length is 2.6 cm; the base is 1.1 by 1.2 cm, with a perforation about 0.2 cm in diameter in each side. Thickness of the sheeting is about 0.03 to 0.04 cm. The interior is filled nearly to the edges of the base with light buff-colored clay, which has been depressed or cut away to provide connections between the perforations and which might have served as a casting core (Fig. 2). Analysis by x-ray fluorescence of the claw surface combined with microscopic examination shows strong presence of gold, copper, and silver. Copper corrosion on the surface indicates that the object has suffered diffusion reactions. Corrosion has affected portions of the junctions between the faces of the claw and has affected the tip and part of the base, where one of the two perforations has been largely obliterated. Unfortunately, it has not been possible to undertake spectrographic analysis to provide technical data for comparison with data from various metal-rich areas of Mesoamerica, but identification of the material as tumbaga, with probably unintentional inclusion of silver, is unquestionable.

The high percentage of tumbaga in metal objects from southern Central America during the period of the Maya Classic suggests this area as the most likely source, and there are, in fact,

two artifacts identical with the Altun Ha specimen in the collection from Coclé in central Panama (4). Unfortunately, the two Coclé objects were purchased, and hence they cannot be directly related to the archeological sequence for the area. The Coclé occupation was once thought to fall entirely in the Post-Classic period, but ^{14}C dates from Panama now indicate a span from A.D. 500 or earlier to about A.D. 1300, with the initial date open to considerable question (5). The data from Coclé provide a fairly solid basis for assuming that metalworking had progressed sufficiently in the area by or before A.D. 500 to have begun to play a role in trade relationships that extended beyond the borders of central Panama. This assumption is supported by the Altun Ha indication that metalurgy in the Coclé region was coeval with the middle portion of the Maya Early Classic, if not earlier. Hence the

Altun Ha discovery provides apparent confirmation of the radiocarbon-dated Panama sequence, as well as evidence of trade ties, however tenuous, linking the Maya with southern Central America at an unexpectedly early time.

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References and Notes

1. D. M. Pendergast, *Archaeology* 18, 210 (1965); *Estud. Cult. Maya* 6, 149 (1967); *Altun Ha: A Guidebook to the Ancient Maya Ruins* (Univ. of Toronto Press, Toronto, Ont., 1969).
2. G. Stromsvik, *Carnegie Inst. Wash. Publ.* 528 (1941), p. 71, fig. 13, b and c.
3. J. E. S. Thompson, *Amer. Antiquity* 30, 343 (1965).
4. S. Lothrop, *Peabody Mus. Mem.* 7 (1937), fig. 183d.
5. S. Lothrop, *Miss. Mus. Volkerkunde Hamburg* 25, 88 (1959).
6. Supported by Canada Council and Harvie Foundation, Calgary. The x-ray fluorescence analysis was made by Mr. Bernard Leech, Curator-in-charge, Conservation Department, Royal Ontario Museum.

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Disintegration of Charged Liquid Jets:

Results with Isopropyl Alcohol

Abstract. *Disintegration processes occurring with charged jets of isopropyl alcohol differ in several respects from results obtained with water. Although bimodal distributions of drop size shift to smaller diameters with increasing electrification for both liquids, the lower surface tension of the alcohol promotes the formation of secondary jets and a fan configuration not observed for water.*

Disintegration of charged liquid jets and subsequent droplet formation have been studied for more than a century. Peculiarities in the patterns of charged jet disintegration and drop formation have recently been described in some detail. Magarvey and Outhouse (1) investigated the breakup of thin water jets under combined electrical, molecular, and gravitational forces. With the onset of charging, the region at which the drops break off from the jet is affected first. With increased charging, the jet forms looping filaments characteristic of a length-extension instability. The drops formed after severing of the filaments have a different size distribution from those formed from an uncharged jet.

Huebner (2), using high-speed photographic techniques, found that charging of cylindrical jets of distilled water reduces the size of drops formed from the jets; the decrease in mean size increases with applied potential. Mean drop size decreases with increasing electrification of jets of isopropyl alco-

hol, partly as a result of the development of secondary jets from the primary jet. A new mode of jet disintegration in a fan-like configuration was observed.

The apparatus used to produce charged liquid jets has an insulated liquid reservoir in contact with one terminal of a conventional high-voltage source. A cylindrical, metal vessel coaxial with the jet collects the effluent and serves as the ground, or return, electrode. Two narrow slots, directly opposite each other in the sides of the collector, allow one to observe and photograph the jet breakup and droplet dynamics. A Wollensak Fastax high-speed motion picture camera synchronized with a microsecond pulse flash lamp permitted direct measurement of drop images in order to determine the sizes of drops formed from electrified jets (2).

The disintegration patterns of jets of isopropyl alcohol differ from those of water in that the former exhibit (i) extensive formation of secondary jets

and (ii) the development of a fan configuration under certain electrical conditions (Fig. 1). For one of the jets of smaller diameter, the sausage instability, which results in drop formation from an uncharged jet (Fig. 1a), increases with slight electrification. Further electrification produces a kink instability (Fig. 1b). Still further increase in electrification results in the length-extension instability (Fig. 1c), which has also been observed with water jets of small diameter (1, 2). At the highest electrification possible without the onset of corona, the circular jet develops a fan-like configuration (Fig. 1d). The length-extension instability occurs with the smallest jets at low and intermediate flow rates and with jets of intermediate size at very low flow rates; it does not occur at all with the largest jets. The fan configuration developed at the higher applied potentials over the range of jet diameters used (0.372 to 1.25 mm).

Upon formation of the kink mode, very fine secondary jets develop at the positions of greatest lateral displacement. Full development of the fan is accompanied by an increase in the number of secondary jets, which form at the end of the fan. These secondary jets, which project outward at large angles with respect to the jet axis, are subject to the same instabilities as the primary jet and disintegrate quickly to form large numbers of small droplets.

As shown in Fig. 2, the reduction in the size of drops formed from the primary jet with increasing electrification and the formation of secondary jets cause a significant decrease in mean diameter compared to that in the case of the unelectrified jet. The orifice produces a bimodal distribution; both maxima usually shift toward smaller drop diameters with increasing electrification. As the applied potential V increased from 15 to 25 kv, and as the jet current i (measured between reservoir and collector) increased with the applied potential from 0.8 to 2.0 μA , the sizes of the larger drops changed very little but the relative number of larger drops produced decreased sharply, while the relative number of smaller drops produced increased commensurately. Many of these drops were smaller than the lower limit of resolution of the optical system. This accounts for the absence of a maximum in the distribution at small drop diameters.