

Fig. 4. Comparison of C^{14} deviations for the half-life 5730 years according to Suess (9) (curve b) with the geomagnetic moment changes (curve a) (6). Dashed portion of the curve represents average changes determined from values in Europe, Central America, and Japan; dotted curve is for changes from Europe only.

values can be detected, which amounts to a shift rate of approximately 120° of longitude in 500 years or 0.24° per year. This value corresponds very well with the values determined on the basis of direct geomagnetic field measurements by geophysical observatories and geomagnetic mapping during the past century (7).

Archeomagnetic measurements of South American pottery (8) show that a similar increase in intensity took place during approximately the same time period. Moreover, when archeomagnetic results from America, Europe, and Japan are taken into account, it is possible to calculate values for the earth's magnetic moment of the archaeological past (6). These values show a very good inverse coincidence (Fig. 4) with secular fluctuations in the production rate of radiocarbon reported earlier by Suess (9). Since archeomagnetic measurements have made it possible to detect the apparently direct dependence between changes of the earth's magnetic moment and changes in the production rate of radiocarbon, any possible influence of the earth's magnetic field during the last 40,000 years can be estimated by conducting magnetic paleointensity measurements on sediments that are datable by the radiocarbon method. The experiments reported here should go a long way toward clarifying the relative effectiveness of the magnetic behavior of the earth and sun and their influence on the production rate of radiocarbon as discussed recently by Libby (10). Finally, there remains the interesting aspect that a redefinition of the mean radiocarbon concentration in the biosphere, in the

light of variations in the production of C^{14} with time, might present a different view of the extent of maximum deviation, which might be cut in half.

V. BUCHA*

*Geophysical Institute of
Czechoslovak Academy of
Science, Prague*

R. E. TAYLOR†, RAINER BERGER
*Department of Anthropology and
Institute of Geophysics, University
of California, Los Angeles*

E. W. HAURY
*Department of Anthropology,
University of Arizona,
Tucson*

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* Present address: Institute of Geophysics, University of California, Los Angeles and San Diego.

† Present address: Department of Anthropology, University of California, Riverside.

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Polywater: An Attempt at Synthesis in a Gas Discharge

Abstract. An attempt to produce polywater in a corona discharge in moist air was unsuccessful. However, the major product produced, nitric acid, has a midrange infrared spectrum which is strikingly similar to that reported for polywater. The Raman spectrum offers a better means of distinguishing between nitric acid and polywater than the infrared spectrum does.

Recently, Lippincott *et al.* (1) have presented evidence that the "anomalous water" studied extensively by Deryagin and Churayev (2) is a well-defined polymeric form of water. Polywater is most commonly prepared by condensing ordinary water in freshly drawn glass capillaries. The small quantities produced by this method have hampered precise characterization of the properties of the material and have led us to consider alternate methods of preparation.

Experiments by Shahin (3) and others have established that the principal charge carriers in a positive corona discharge in moist air are species of the form $(H_2O)_nH^+$, where n has been observed to vary from 1 to 9 under typical conditions. The detailed structure of the ions has not been determined; however, both simple hydration and more complicated bonding schemes have been suggested (4). The similarity in the form of these species to the polymeric form proposed by Lippincott *et al.* suggested that polywater might be a product of a positive corona discharge in moist air. Fowkes (see 5) has observed that strong electric fields are known to exist at freshly drawn glass surfaces. It has been suggested that the role of the electric field is to attract water molecules to the glass surface where the molecular arrangement provides a "pattern" for the formation of polywater by a sort of epitaxial growth. We speculated, however, that the surface fields might be adequate to produce air breakdown in the capillary and that the polywater could be formed in the resulting discharge.

We initiated experiments designed to collect and identify the products of a positive corona discharge in moist air. The apparatus used consisted of an O-ring-sealed Pyrex vessel with an internal volume of about 1 liter enclosing a corona device of coaxial cylinder geometry. The relative humidity in the vessel was maintained at 100 percent

by supplying water from an attached reservoir held at the same temperature as the vessel. The device was fitted with Irtran-2 (Eastman Kodak) windows so that the discharge products could be monitored in situ by transmission infrared spectroscopy.

Figure 1A shows the midrange infrared spectrum obtained in situ on a Beckman IR-10 infrared spectrometer for a sample of moist laboratory air subjected to a 100- μ a discharge for 2 hours. Figure 1B shows Lippincott's reported polywater spectrum, and Fig. 1C shows a spectrum of a film of H_2O held between two Irtran-2 windows. There are strong similarities between Lippincott's spectrum and our own, especially if some water absorption is superimposed on the polywater spectrum, as would be the case in a dilute solution. A more recent spectrum reported by Page *et al.* (6) bears an even more striking resemblance to our spectrum.

Despite the similarities, however, we do not believe that our sample contains polywater. It has been known for some time (7) that nitrogen oxides are common products of a discharge in air and that, in the presence of water, nitric acid solutions are formed. Figure 1D shows the spectrum of a 35 percent solution of HNO_3 in H_2O obtained for a sample held between Irtran-2 windows. The spectrum is identical to that in Fig. 1A and is taken along with the experimental conditions as conclusive evidence that most of the material produced in the corona discharge is a nitric acid solution.

In additional experiments the corona device was operated in both moist O_2 and N_2 atmospheres. Shahin (3) has shown that in these cases, as in the case of moist air, the predominant charge carriers are hydrated protons $(H_2O)_nH^+$. In N_2 the discharge was maintained for 2 days without development of any significant absorption in the infrared spectrum. Operation of the device in moist O_2 for about 1 day produced a spectrum similar to that in Fig. 1A but it lacked the absorption band at 1400 cm^{-1} .

The absorption bands in Fig. 1, A and D, can be identified with the known spectral features of water (8) and nitric acid (9). The spectrum obtained for the products from the moist O_2 discharge can be attributed to a mixture of water and ozone (10). In all of the spectra the absorption band at 1100 cm^{-1} may be a composite peak of ab-

sorptions due to H_3O^+ (11), ozone, and possibly sulfate ions (12) produced by the action of nitric acid or ozone on Irtran-2 (zinc sulfide).

Because of the close match between

known nitric acid peaks and the polywater peaks reported by Lippincott in the midrange infrared spectrum, it is impossible to establish by this means that polywater is *not* formed in a co-

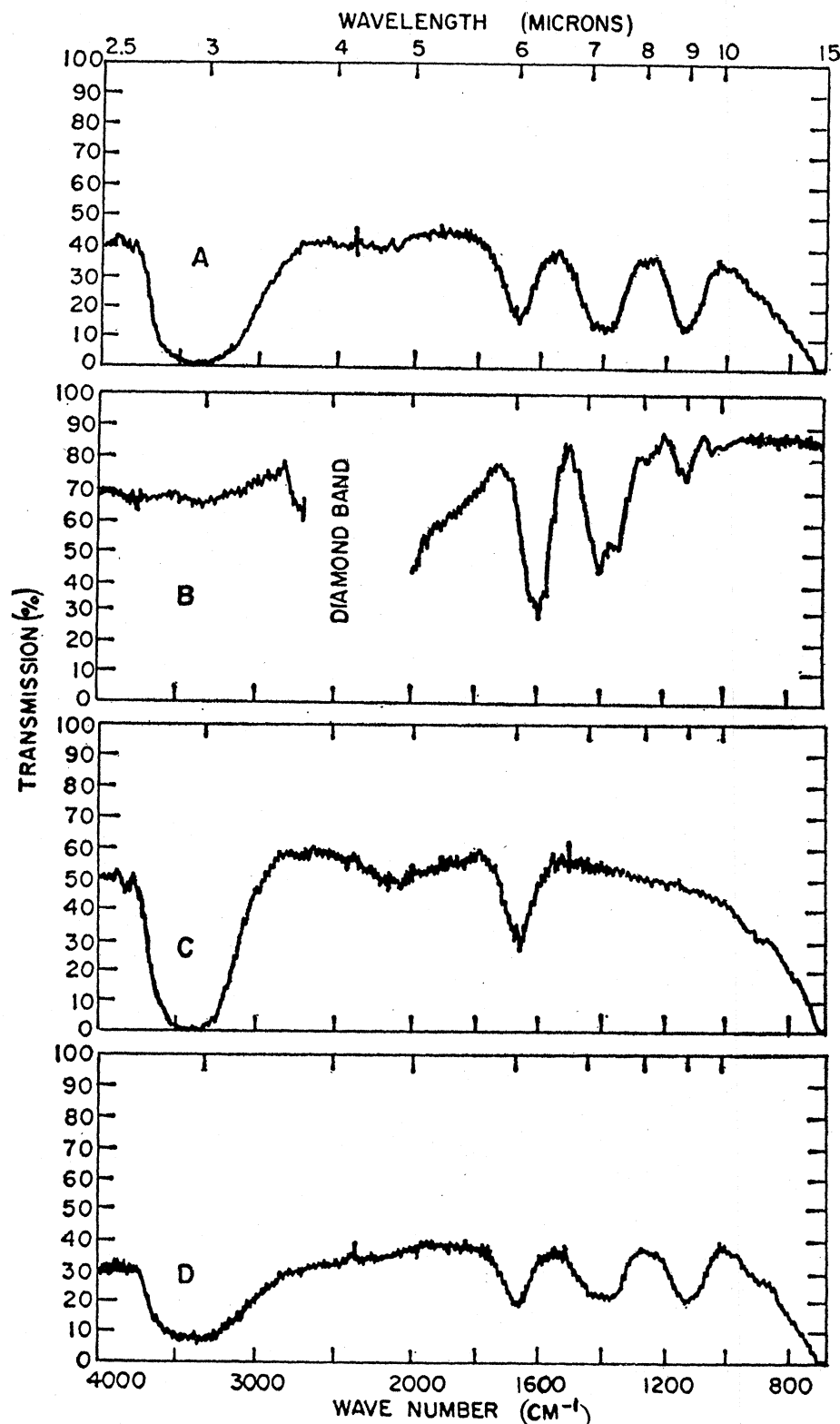


Fig. 1. (A) In situ infrared spectrum of products of corona discharge in moist air. (B) Polywater spectrum reported by Lippincott *et al.* (1). (C) Infrared spectrum of H_2O . (D) Infrared spectrum of a 35 percent solution of HNO_3 .

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.

ALGIRD G. LEIGA
DENNIS W. VANCE
ANTHONY T. WARD

Xerox Corporation, Research
Laboratories, Rochester, New York

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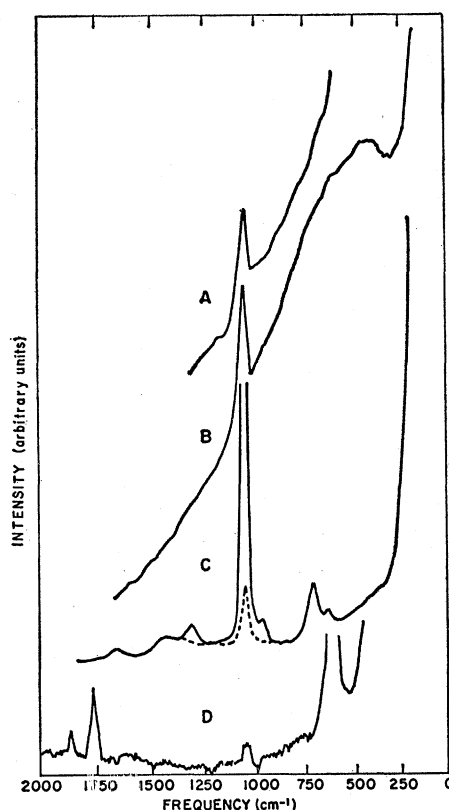


Fig. 2. (A) Stokes region Raman spectrum of products of corona discharge in moist air (incident radiation electric vector polarized perpendicular to the direction of observation of scattered light; the 1050-cm^{-1} line does not appear for parallel polarization). (B) Stokes region Raman spectrum of a 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