HO. Cox *et al.* (*17*) give 2.8×10^{-14} cm^3 sec^{-1}; C. J. Howard and K. M. Evenson [*J. Chem. Phys.* **64**, 4303 (1976)] give 1.5×10^{-14} cm^3 sec^{-1}. Values obtained by D. Davis and R. T. Watson and by J. S. Chang, C. Steen, and F. Kaufman [Appendix A in (*3*)] are 1.6×10^{-14} and 2.2×10^{-14} cm^3 sec^{-1}, respectively. We have adopted the temperature-dependent rate of $8 \times 10^{-13} \exp(-1200/T)$ cm^3 sec^{-1}.
12. The reaction between trichloroethylene and HO is $\sim 2 \times 10^{-12}$ cm^3 sec^{-1} [see, for example, table A.1 in Appendix A of (*3*)].
13. P. J. Crutzen, I. S. A. Isaksen, and J. McAfee (*J. Geophys. Res.*, in press) have calculated that about 12 percent of the methyl chloroform released will reach the stratosphere. They have also calculated the loss of O_3 due to methyl chloroform production increasing at the present rate.
14. In the model we used the implicit finite difference technique with conservation conditions applied to each family of atmospheric components, a technique similar to that described by R. P. Turco and R. C. Whitten [*J. Geophys. Res.* **79**, 3179 (1974)]. The families are as follows: $O_x = O_3$, NO_2, and O; NO_x = N, NO, NO_2, NO_3, N_2O_5, and HNO_3; HO_x = H, HO, and HO_2; ClX = Cl, ClO, HCl, and $ClONO_2$. The concentrations of $CFCl_3$, CF_2Cl_2, and CH_3CCl_3 were also allowed to vary with time and altitude, as were the concentrations of CH_3Cl, CO, N_2O, CH_4, and H_2O_2. Each constituent was allowed to vary subject to the following boundary conditions. The mixing ratios of O_2, H_2, CO_2, and H_2O were kept fixed. Constant flux boundary conditions were assumed for O_x, ClX, and NO_x. The surface mixing ratios of N_2O, CH_4, CO, and CH_3Cl were kept constant at typical tropospheric values. Quasi steady-state was assumed for determining the mixing ratios of short-lived species, for example, NO, H, and HO. The reaction rate data were taken largely from the compilation of recommended values by the National Bureau of Standards [R. F. Hampson and D. Garvin, "Chemical, kinetic and photochemical data for modelling atmospheric chemistry" (Technical Note 866, National Bureau of Standards, Gaithersburg, Md., 1975)] and from the report of the National Academy of Sciences (*3*); a value of 5×10^{-11} cm^3 sec^{-1} was adopted for the uncertain rate constant for $HO + HO_2 \rightarrow H_2O + O_2$. Cross sections for photolysis were taken from J. C. McConnell and M. B. McElroy [*J. Atmos. Sci.* **30**, 1465 (1973)] and from (*3*) except for methyl chloroform; the data for this compound were kindly supplied by Dr. F. S. Rowland (personal communication). Values of the solar flux as a function of wavelength were taken from (*3*). The photodissociation rate coefficient *J* was approximated by a 24-hour average at 30°N for equinox. This approximation tends to exaggerate the $ClONO_2$ concentration and minimizes O_3 losses.
15. The results presented here were obtained with the eddy diffusion profile developed by D. M. Hunten [*Proc. Natl. Acad. Sci. U.S.A.* **72**, 4711 (1975)].
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18. We calculated the average value, assuming that methyl chloroform has a latitudinal variation similar to that for F-11 as reported by J. E. Lovelock, R. J. Maggs, and R. J. Wade [*Nature (London)* **241**, 194 (1973)]. This calculation gives a value of 2.0 for the interhemispheric ratio. This can be compared with a value of 2.7 obtained by taking the measurement of methyl chloroform referred to in the text for 51.7°N and 34°S as being representative of the Northern and Southern hemispheres, respectively.
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21. Here τ_c = the total amount in the atmosphere in the steady state divided by the input flux.
22. The time constant for release (τ_R) is defined by the expression: release rate = $A \exp(t/\tau_R)$, where *t* is time and *A* is a constant.
23. We have used the F-11 measurements of Lovelock *et al.* (*18*). A similar value for τ_I has been obtained by F. S. Rowland (personal communication).
24. Using low-altitude meridional wind fields discussed by E. R. Reiter [in *Atmospheric Transport Processes*, Part 1, *Energy Transfers and Transformations* (Atomic Energy Commission, Washington, D.C., 1969), p. 14], we obtain an estimate for τ_I of 8 months.
25. A. Walton, M. Eergin, and D. D. Harkness [*J. Geophys. Res.* **75**, 3089 (1970)] found that $\tau_I \simeq 4$ years is in agreement with data on ^{14}C in the troposphere.
26. Y. L. Yung, M. B. McElroy, S. C. Wofsy [*Geophys. Res. Lett.* **2**, 397 (1975)] obtained $\tau_c \simeq 3$ years, implying $\tau_I \simeq 1$ year. However, the global inventory calculated on this basis would be too small by a factor of about 2.
27. The tropospheric HO values that we have obtained are $\simeq 5 \times 10^5$ cm^{-3}. Ground values are lower than those given by some other models [S. C. Wofsy, *Annu. Rev. Earth Planet. Sci.* **4**, 441 (1976)] but are in reasonable agreement at other altitudes. However, they are not in disagreement with HO values suggested by P. Warneck [*Tellus* **26**, 39 (1974)], who investigated the effects of heterogeneous reactions occurring on the surfaces of particles terminating $HO\text{-}HO_2$ cycles. W. Seiler and U. Schmidt [in *Proceedings of the International Conference on the Structure, Composition and General Circulation of the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations*, N. J. Derco and E. J. Truhlar, Eds. (Atmospheric Environment Services, Downsview, Ontario, Canada, 1974), p. 192], on the basis of interhemispheric CO mixing ratios, suggested that low to intermediate HO densities should obtain. In view of the fact that the HO densities we calculate are average densities, they are not in conflict with measurements such as those of D. Perner, D. H. Ehhalt, H. W. Pätz, V. Platt, E. R. Roth, and A. Volz [*Geophys. Res. Lett.* **3**, 466 (1976)] obtained at Julich (51°N, 6°E).
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29. The steady-state value of ΔO_3 that we obtain, using the profile of eddy diffusion coefficients of D. H. Ehhalt, L. E. Heidt, R. H. Lueb, and E. A. Martell [*J. Atmos. Sci.* **32**, 163 (1975)], is 9.6 percent.
30. Obviously, if the values of HO that we have used do not obtain and are adjusted, then the ΔO_3 values calculated must be modified. Similarly, the conclusions may be modified by a change in the rate constant for the reaction of HO with methyl chloroform.
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28 March 1977; revised 11 November 1977

Phytolith Analysis of Archeological Soils: Evidence for Maize Cultivation in Formative Ecuador

Abstract. *Soil samples from the archeological sites of Real Alto and OGCh-20, Santa Elena Peninsula, Ecuador, show the presence of cross-shaped silica bodies identifiable as maize* (Zea mays *L.*) *phytoliths by size comparison with known wild grass and maize phytoliths. These results support arguments for the cultivation of maize at 2450 B.C. in coastal Ecuador.*

In attempting to reconstruct the subsistence systems of prehistoric peoples, archeologists have come to rely on techniques such as soil flotation and pollen analysis to recover the remains of utilized wild plants and cultigens. The recovery of phytoliths, silica bodies present in the epidermal cells of some plant groups, is a technique less known to American archeologists. It has been used in Europe, the Middle East, and Japan to indicate the presence of cultivated grasses in sites with poor botanical preservation (*1*). During the University of Illinois excavations of the Valdivia culture (3000–1500 B.C.) site Real Alto and the Machalilla (1500–1000 B.C.) site OGCh-20 in the Santa Elena Peninsula, Ecuador, soil samples were taken for phytolith analysis to test for the presence of maize (*Zea mays* L.) at these sites (*2*). Preliminary efforts to distinguish maize phytoliths from phytoliths present in the native grasses of the peninsula have given positive results. Cross-shaped phytoliths distinguishable as maize have been found in ten archeological soil samples.

As plants grow and take up water from the soil, they absorb dissolved minerals, including silica. Silica is deposited in the epidermal cells of the leaves, both across the veins and between them. In many taxa, distinctively shaped bodies are formed when the silica completely fills a cell (*3, 4*). In the grasses, phytolith types can be associated with distinctive tribes or genera and distinguished from herbaceous or tree phytoliths. Identification of the parent plant from phytoliths deposited in the soil is possible, particularly when quantitative data on the frequency of occurrence of the types are available (*5*). Agronomists and soil scientists have used the occurrence of phytoliths deposited in soils as the result of plant decay or burning to determine the composition of an area's flora in previous epochs. Areas of grassland vegetation can be distinguished from those of woodland on this basis (*6*).

Leaves of maize and ten genera of wild grasses occurring in coastal Ecuador were used as comparative materials in this study. During the 1975 rainy season on the Santa Elena Peninsula, I collected native grasses and identified them to genus. I selected from this collection the genera *Aristida, Bouteluoa, Cenchrus, Chloris, Dactyloctenium, Eleusine, Eragrostis, Panicum*, and *Ischaemum* for this study. *Tripsacum* grown in Illinois was also included. These genera were selected to include a variety of phytolith types, including the cross-shaped type which characterizes maize (*4*). The

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Table 1. Percentages of cross-shaped phytoliths in each of the four size categories for three genera of wild grasses, for each race of maize studied, for the average of these races of maize, and for the archeological material. The size categories are: small, 6.87 to 11.40 μm; medium, 11.45 to 15.98 μm; large, 16.03 to 20.56 μm; and extra large, 20.61 to 25.19 μm,

Material	Size			
	Small	Medium	Large	Extra large
Wild grasses				
Tripsacum	25	75	0	0
Cenchrus	20	80	0	0
Eleucine	100	0	0	0
Races of maize				
Mischa	12	63	25	0
Mischa-Huandango	0	46	52	2
Sabanero	7	81	12	0
Morochon	9	50	41	0
Purple flint	77	23	0	0
(C) Patillo	6	79	15	0
Canguil	12	74	14	0
(O) Patillo	0	50	48	2
Cuzco	0	25	62	13
Maize, average	13	55	30	2
Archeological	12	52	36	0

maize material used for comparison was grown in Illinois from seed collected in Ecuador. Nine races were included in the comparative study (*7*).

The phytoliths of all the comparative materials exposed through epidermal peels of mature leaf segments were studied at a magnification of 312. I examined 100 phytoliths occurring across the leaf veins for each genus and determined the overall percentage occurrence of the cross-shaped type. This type is defined here as phytoliths having a dimension of N by N to N by (N + 2), with indentations on at least three sides (*8*). Only the genera *Zea, Tripsacum, Cenchrus*, and *Eleusine* had cross-shaped phytoliths. This type of phytolith made up an average of 51 percent of the across-the-vein phytoliths in the *Zea* races, but less than 13 percent for the other genera.

Since *Zea, Tripsacum, Cenchrus*, and *Eleusine* all are characterized by cross-shaped phytoliths, I hypothesized that phytolith size could be used to distinguish maize cross-shaped phytoliths from those of the other grasses. Table 1 shows the size distribution of cross-shaped phytoliths in the races of maize studied. The races Mishca-Huandango, Patillo from Otavalo, and Cuzco Ecuatoriano are distinctive in forming the largest cross-shaped phytoliths observed. The race purple flint is unique in forming predominately small cross-shaped phytoliths. The other races studied show similar cross-shaped phytolith size distributions. From the data on phytolith size variation between races of maize, an average cross-shaped phytolith composition for maize was calculated. Table 1 shows the comparison of the size distribution of the cross-shaped phytoliths in maize with the size distribution of cross-shaped phytoliths in the grasses *Tripsacum, Cenchrus*, and *Eleusine*. Maize can be distinguished by the presence of large or extra large cross-shaped phytoliths, which do not occur in the other genera.

The archeological soil samples selected for phytolith extraction came from securely dated strata in various types of occupation areas at the Real Alto and OGCh-20 sites. Soil from hearth areas, living floors, storage or garbage pits, and general midden deposits was included. Most samples came from Valdivia II–III strata (2450–2150 B.C.), with a few samples from later Machalilla deposits (1500 B.C.) (*9*). The samples were processed with the procedure published by Rovner, with some minor modifications (*5, 10*). One hundred phytoliths were examined for each of 17 samples. All samples contained phytoliths of varying types, but only 12 contained cross-shaped phytoliths, for a total of 42 of this type. The size distribution of the cross-shaped phytoliths from the archeological soil samples is shown in Table 1. Although cross-shaped "archeological phytoliths" of the small and medium size range cannot be identified definitely on the basis of size as maize, the archeological phytoliths in the "large" category can be distinguished as maize rather than wild grass. Thirty-six percent of the archeological cross-shaped phytoliths fall within the maize category. These phytoliths of the maize category came from ten samples, including hearths, floors, and pits from Valdivia II–III and Machalilla strata. The smaller types could also have come from maize or from wild grasses used as roof thatch or bedding.

The phytolith classification scheme and the conclusions presented here are preliminary tests of a promising method for identifying the presence of maize in archeological contexts. The method needs to be tested further with other grasses and to explore other distinguishing criteria. Phytolith analysis is particularly promising for areas where the preservation of archeological macrobotanical remains or pollen is poor. Because in most cases it can be assumed that grass litter decayed in situ, such as in a pit or on a floor, there is less danger of phytoliths being blown in, as is often the concern with pollen (*11*). Since phytoliths come from vegetative and flowering structures, their presence at the Real Alto and OGCh-20 sites cannot be explained by occasional importation of a few cobs, but instead implies on-site cultivation of maize by at least 2450 B.C.

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2. All dates are in uncorrected carbon-14 years, quoted from D. Lathrap [*Ancient Ecuador: Culture, Clay, and Creativity 3000–300 B.C.* (Field Museum of Natural History, Chicago, 1975)]. Dr. Donald W. Lathrap headed the Chanduy Valley Project. Jorge G. Marcos supervised excavations at the Real Alto site. Ron Lippe (University of Wisconsin, Madison) supervised excavations at OGCh-20. Funding for the field project was provided by the National Science Foundation and the Wenner-Gren Foundation.
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25 July 1977