populations in question, a discriminant function is valuable. The seven measurements listed in Table 1 were used in such a function, which assigned all but 3 of the 80 human and chimpanzee specimens of our two samples to the correct population, producing little overlap in scores. To indicate the degree of discrimination, the means and standard deviation of the individual scores were: chimpanzee, X 99.77, s.d. 13.19; Homo, X 61.42, s.d. 9.23.

Kanapoi Hominoid 1, with a discriminant score of 59.4, falls very close to the human mean and at a point where the probability of its occurrence in the chimpanzee population approximates .001. The Paranthropus specimen has a score of 63.9, which also falls beyond the observed range of the sample of 40 chimpanzees. However, aspects of the data suggest that, while statistically excluded from a chimpanzee population, the Paranthropus specimen is distinctly less like a hominine than is the specimen of Kanapoi Hominoid 1. Metrical and morphological data appear to be in agreement for both fossils.

On the basis of our interpretation of the geological and faunal data, Kanapoi Hominoid 1 is the earliest Pleistocene representative of the Hominidae yet found. To us the most interesting fact is the difference of form and size of the new fossil from the Kromdraai fragment identified as Paranthropus robustus. If the latter assignment is correctand there is at present no reason to doubt it-then it is quite unlikely that Kanapoi Hominoid 1 was a member of the same lineage; although earlier in time it is more hominine. Napier (10)has presented evidence that Australopithecus s.s. and Paranthropus were widely different in the structure of the pelvic bones and the proximal ends of the femora, to a degree indicating a difference in gait, with Australopithecus being much closer to modern man. This evidence supports the view of Robinson (11) and others that Australopithecus was a hominine. Kanapoi Hominoid 1 suggests that corresponding differences in the arm may have existed within the Hominidae during the earlier Pleistocene. All this points to the possibility that Kanapoi Hominoid 1 may prove to be Australopithecus, and the comparatively large size of Kanapoi Hominoid 1 is compatible with this possibility. The dimensions of the proximal end of the humerus of Australopithecus from Sterkfontein (12) are within the observed range of modern man; in fact there are individuals in our sample of man on whom measurements of this specimen and of Kanapoi Hominoid 1 can be duplicated almost exactly.

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## **Radiocarbon Dating of Biogenetic Opal**

Abstract. Approximately 75 grams of biogenetic opal were isolated from 45 kilograms of soil by employing gross particle-size and sink-float specific gravity fractionation procedures. After pretreatment of the sample to remove extraneous organic and inorganic carbon contaminants, the carbon occluded within opal phytoliths was dated at  $13,300 \pm 450$  years before the present. Therefore, biogenetic opal is stable for relatively long periods.

The feasibility of utilizing opal phytoliths isolated from soils as a C14 source when other materials are unavailable or undesirable for dating purposes has been proposed (1, 2). This report describes a procedure for dating carbon occluded within opal phytoliths without apparent contamination from extraneous forms of soil carbon.

Opaline constituents were isolated from the surface horizon (0 to 18 cm) of a well-drained Brunizem soil (Warsaw silt loam, site CH-34, Lab. No. 10539) which was sampled on a nearly level terrace along the Mad River Valley in west-central Ohio. The age of the valley train sediments from which the soil developed is 14,000 to 18,000 years before the present (3). Based on the vegetative history of the area (4), the physical and chemical properties of Warsaw soil, and its opaline constituents, it is concluded that this soil developed under a prairie vegetation.

From opaline analysis of this profile, it was observed that the distribution of opal phytoliths (20 to 50  $\mu$ ) (expressed on a total soil basis) decreases with depth as follows: 0.56 percent, 0 to 18 cm; 0.23 percent, 18 to 33 cm; 0.15 percent, 33 to 48 cm; and 0.04 percent, 48 to 63 cm. This amounts to a total accumulation of 22,430 kg of opal per hectare for the 0- to 63-cm portion of soil profile [20,466 lb/acre (25-inch depth) based on a weight of 2 million pounds of soil per acre (6-inch depth)]. If one assumes an annual deposition of 16.4 kg of opal per hectare (15 lb/acre) as previously estimated (5), it would require about 1350 years to accumulate the quantity of opal found at this site. Similar calculations for a Brunizem soil in Illinois suggests that approximately 5000 years of grass vegetation, presumably since the Climatic Optimum, would be required to accumulate the opal found at that site (5). Based on this evidence, it was anticipated that the radiocarbon age of opal isolated from Warsaw soil would be between 1000 and 1500 years before the present.

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computations, and E. Delson, A. Charles, and P. Ward for general assistance.

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The following laborious and timeconsuming procedures were employed to fractionate and purify approximately 75 g of opal from 45 kg of soil. The bulk sample was crushed to < 2mm in a mechanical crusher (Hasco-Asplin), dispersed with 1 g of Calgon

(commercial hexametaphosphate) per 90 g of soil, and agitated for 8 hours in a large mechanical mixer (7 kg of soil and 36 liters of water per batch). A preliminary particle-size fractionation of the  $< 20-\mu$  fraction was achieved by conventional sedimentation-decantation techniques (6) prior to removal of soil organic matter by hydrogen peroxide  $(H_2O_2)$  oxidation. Two 50-liter settling containers, sufficiently tall to permit a particle fall of 45 cm and a sedimentation time of about 27 minutes at 10°C, were used for this separation. The sedimentation-decantation procedure was repeated seven times. The > 20- $\mu$  sediment was then treated with 4.5 liters of 30 percent  $H_2O_2$  and continuously mixed for 4 hours at about -6.6 °C. The oxidation procedure was repeated twice prior to redispersion of the >  $20-\mu$  fraction in Calgon and final particle fractionation of the sediment as described above.

The > 20- $\mu$  total mineral fraction was dried at 110°C, and biogenetic opal was isolated from this fraction by a sink-float specific gravity technique. Approximately 500 g of this >  $20-\mu$ fraction was thoroughly mixed with 12 liters of a nitrobenzene-bromoform solution (specific gravity, 2.30). Sufficient time was allowed for opaline constituents to float to the surface of the heavy liquid from which they were removed and then purified by a centrifugation-decantation method similar to that described by Jones and Beavers (5). These procedures were repeated until the yield of opal reduced sharply. The opal isolate was washed thoroughly with acetone to remove the heavy liquid as an impurity.

Final preparation of opal for carbon dating consisted of treating the sample with boiling 1N chromic acid and cold 30 percent  $H_2O_2$  to reduce the danger of contamination of occluded carbon with extraneous sources of soil carbon. Effectiveness of such procedures have been discussed previously (2). The sample was then pulverized to a fine powder by grinding it for 8 hours in a mortar with an automatic pestle. It was given a final 12-hour treatment with 6N HCl at room temperature to remove possible carbonate contamination. After removing excess acids from the sample with distilled water and then drying it for several days in an oven at 70 to 150 mm-Hg and 70°C, the absence of carbonates was verified by x-ray powder patterns of the treated 7 APRIL 1967

specimen. Infrared spectra of opal samples treated in a similar manner (2) suggest no evidence that bromoform remained as a contaminant after this pretreatment.

A 60-g sample of opal that contained 1.30 percent carbon, or a total of about 0.75 g, was dated by the radiocarbon method by Isotopes, Inc., Westwood, New Jersey, and a carbon date (I-2277) of  $13,300 \pm 450$  years before the present was obtained. This places the age of the opal considerably older than was anticipated and provides evidence that opal phytoliths are stable under these soil weathering conditions for at least 13,000 years. Apparently those opal phytoliths containing carbon occlusions that are resistant to the oxidizing pretreatment were deposited shortly after the close of the last glacial period in Ohio (3). Evidence that such opaline constituents are in fact authigenic lies in their marked decrease with depth in the profile. Similar depth distributions have been established for a number of other Ohio soils.

Additional work is underway to understand the apparent anomaly between the anticipated and obtained carbon dates. It is known that at least 50 percent of the occluded organic constituents are readily oxidizable (2). However, it is not known whether the oxidation reaction is of equal magnitude for all opal bodies or whether organic occlusions in some specimens (presumably more recently deposited open framework structures) are completely digested while others remain essentially inert. Upon oxidation, such a phenomenon would favor preservation of older carbon occlusions at the expense of younger ones, and thus may account in part for the older carbon date obtained. Preferential oxidation would not affect the validity of the date as an estimate of the minimum age of the valley train sediments. It would, however, preclude the use of such dates to reconstruct ecologically the major period of grass vegetation at a particular site.

At this time data are insufficient to speculate which of the above interpretations is valid. When additional information is obtained to evaluate the factors affecting radiocarbon dating of opal, this material may become a very useful C14 source.

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## Osmotic Mechanism and **Negative Pressure**

Abstract. When solute molecules are confined, they exert a positive pressure on the barrier. If this is simply the free solvent surface, balance of forces requires the solvent to attain an equal negative hydrostatic pressure. This offers a sufficient explanation for the reduction of the vapor pressure over a solution.

As a result of work on mangroves and other vascular plants, osmotic relation between parenchyma cells and the xylem sap has been defined. As had been predicted, the osmotic pressure of the cells is indeed balanced by a hydrostatic tension (equivalent to negative pressure) in the nearly saltfree xylem sap. These studies have suggested a mechanism of osmosis different from what is generally postulated (1). In this study I neglect gravity, and denote an outward-directed force as positive and an inward-directed force as negative.



Fig. 1. (Left) Diagram of a 1 molal solution in a semipermeable net surrounded by water; (center) water removed to coincide with net; (right) net removed. Pressure in atmospheres. The arrows indicate the osmotic pressure of the solute molecules against the net or solvent boundary.