

*Anna G. J.*

# RESEARCH REPORT

## Phosphate Content of Ancient Pots as Indication of Use

by G. DUMA

Budapest, Hungary. 4 p 70

### PHOSPHORUS AS A COMPONENT OF CLAYS

Clays, the raw materials for the manufacture of pottery, consist mainly of fine particles and minerals—primarily from igneous rocks—that have resisted weathering. Almost all igneous rocks contain phosphorus-bearing minerals, and therefore so do clays and the pottery made from them. In soil layers on or near the surface, microorganisms decompose the phosphorus-bearing minerals in clays, causing phosphate ions to be built into plant cells and subsequently, through plants, to reach other living organisms as well. Phosphorus plays an important part in the makeup of all living organisms. Consequently, in soil layers on or near the surface, where there are many living organisms and substances of organic origin, the quantity of phosphorus generally exceeds by far that of the underlying layers. The phosphorus content of the surface layers is further augmented by the formation of new phosphates and phosphorus-bearing minerals through the action of phosphoric acid (a characteristic product of the decomposition of organic substances [Walcher 1928, Specht 1937, Lengyel and Nemeskéri 1964]).

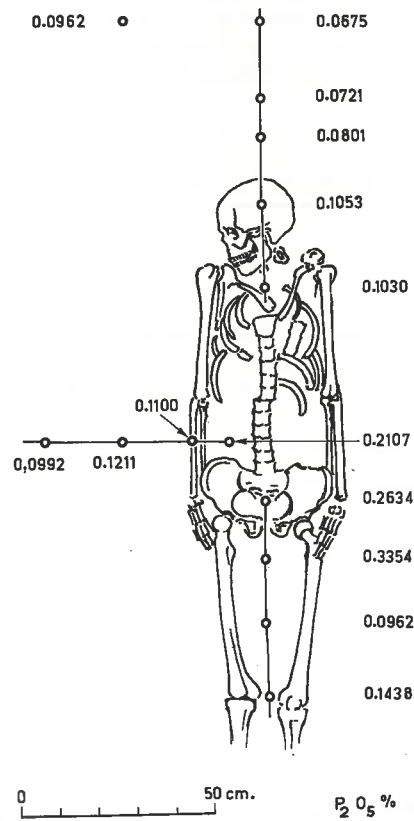
Adsorption and ion exchange are also important in the fixation of phosphate ions in the soil. Bonds with colloidal particles of the soil readily develop with clay minerals (Black 1942, Coleman 1944, Dean 1949, Hall and MacKenzie 1947, Hemwall 1957, Hendriks and Dean 1947, McAuliffe 1947, Stout 1939). In the fixation of phosphate ions to various clay minerals, it is very difficult to differentiate between ion exchange, adsorption, and chemical bonding (Jasmund 1951). Phosphate ions become bonded to the minerals of the soil within a very short time; hence their mobility is severely limited (Stoye 1950). Furthermore, the bonds between phosphate ions and individual soil components are very strong. The considerable stability of phosphates in the soil and the fact that most dissolved phosphates and phosphate ions again form not very soluble phosphates and phosphate ions ensures that the phosphorus content of the soil will not be exhausted and, moreover, will in certain cases increase. In the absence of human activity, the catabolic and anabolic processes remain, with some

exceptions, in equilibrium (Stefanovits 1963, Lorch 1941a). Enrichment of the phosphate content of the soil in restricted areas is due to local biological factors and is in most cases of anthropogenic origin (Jakob 1951), attributable to human and animal vital processes (Utescher 1948). Phosphate enrichment of the soil surrounding a 6th-century skeleton excavated at Kishomok by I. Bóna is diagrammed in Figure 1.

### ARCHAEOLOGICAL APPLICATIONS

In view of the limited mobility and strong bonding of phosphate ions, changes in the phosphate content of the soil can be employed, in certain cases, for archaeological determinations. Soil tests for archaeological purposes were made for the first time in 1931 (Arrhenius 1931, 1935). The scientific results achieved since then have proved that this method is suitable for the detection of the presence of man in cultural layers from all epochs, and it

FIG. 1. Phosphate enrichment of the soil surrounding a skeleton from a 6th-century grave (Kishomok, grave no. 89; excavated by I. Bóna in 1966).



has been widely used for such purposes (see Bleck 1965; Cook and Heizer 1965; Cornwall 1958; Dauncy 1952; Felgenhauer and Sauter 1959; Frauendorf and Lorch 1940; Geiger 1936; Grimm 1962; Guyan 1952; Jakob 1951, 1952, 1954, 1955; Lorch 1939a, b, 1940, 1941a, b, 1943, 1944, 1951, 1952; Sauter 1959, 1967; Schmid 1958; Schwarz 1967; Solecki 1951; Stoye 1950, 1955; Uzsóki 1959).

Changes in the phosphate content of the soil can also serve as clues to the original purpose of a pot. By further developing the method long used by archaeologists, attempts have been made (Bleck 1965; Jakob 1954, 1955; Uzsóki 1959) to determine the original purpose of a pot on the basis of the phosphate content of earth samples taken from within the pot or (Jakob 1955) from its inner wall. (The conclusions as to the nature of the original contents of the pot are in some cases [e.g., Jakob 1954] somewhat too far-reaching.) However, in order to draw conclusions as to the original purpose of a pot (i.e., whether it once contained an organic substance) on the basis of the phosphate content of the earth inside it, one must compare that earth sample with one of natural phosphate content—that is, one identical with the sample from inside the pot but uncontaminated by the organic substances originating in the foodstuff it presumably once contained. For this reason, reliable results can only be obtained in the case of a pot found in a known environment and containing undisturbed earth material. In view of the problems raised by this restriction, an approach independent of the environment is needed. Chemical analysis of the pottery itself is such an approach.

### A NEW APPLICATION

Phosphorus, like all the other mineral components of clays, becomes uniformly distributed throughout the deposit in the process of its formation. In soil layers on or near the surface, however, phosphorus generally becomes concentrated in pockets (Rautenberg 1934–35). Therefore, if the raw material for pottery is extracted from layers on or near the surface, the distribution of phosphorus in it will not be uniform. The process of production, however, and particularly the firing, can be expected to spread the phosphorus evenly throughout the finished pot. Chemical analyses of both contemporary and ancient unglazed pottery tend to bear out this hypothesis (see, for example, Fig. 2). When phosphate content is found to vary within a given pot, then, some contact with substances of organic origin can perhaps be assumed.

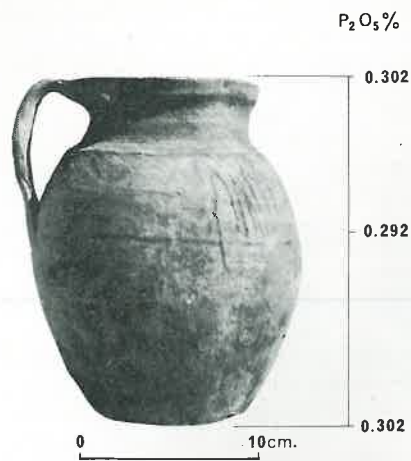


FIG. 2. Phosphate content of a pitcher found in a 6th-century grave (Környe, grave no. 41; excavated by I. Erdélyi and Á. Salamon in 1955) and containing no organic substances.



FIG. 3. Phosphate content of a pot from a 16th-century grave (Környe, grave no. 115; excavated by I. Erdélyi and Á. Salamon in 1955), showing enrichment from top to bottom.

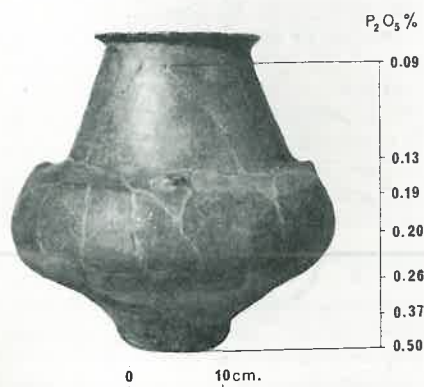


FIG. 4. Phosphate content of a pot from a pre-Scythian grave (Mezőcsát, grave no. 29; excavated by E. Patek in 1958-63), showing enrichment from top to bottom.

In much of the ancient unglazed pottery I have examined, the phosphate content increases, in a given pot, from the brim towards the bottom (Figs. 3, 4). This phenomenon has been observed even in pots the parts of which were found scattered, leaving no doubt that the phosphate enrichment derived from the time when the fragments still formed an integral whole. Rarely, pots were found in which the highest phosphate content was around the brim (Fig. 5). In all of these cases, however, it could be shown that the phosphate enrichment was due to adjacent organic substances.

The apparent porosity (water-absorbing capacity) of pottery is known to decrease with increase in firing temperature. At the temperatures at which ancient unglazed pots were probably fired, porosity would still be so high as to allow liquids to pass through them. Both the material of the pot and the surrounding soil could thus have become imbued with the organic substance the pot contained or the products of its decomposition. It has repeatedly been observed that the phosphate content of the soil in the immediate vicinity of a pot is often higher than in the surrounding area and in some cases considerably higher than in the earth contents of the pot (Jakob 1954, Uzsóki 1959). The results of my own studies (see Table 1 for illustrative examples), showing for used pots a regular increase in phosphate content from top to bottom in (a) the earth contents of the pot, (b) the soil surrounding it, and (c) the pot itself, make it clear that the phosphate enrichment observed can be attributed to an organic substance the pot once contained.

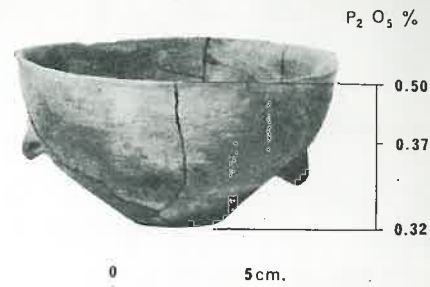


FIG. 5. Phosphate content of a cup from an early Copper Age grave (Oszentiván-Tiszassziget, grave no. VIII. 3; excavated by L. Kutzián in 1960), showing enrichment at brim due to an adjacent animal bone.

If phosphate enrichment by an organic substance once contained by the pot is to persist over long periods underground, then it must be the case that clays, even when fired, are able to bind phosphate ions permanently. Experiments designed to test this assumption and to determine the factors that influence such bonding were undertaken (Duma 1968, 1969). Studies were made of the products of firing of the raw materials of pottery at various temperatures. Since raw materials vary in their content of the minerals that participate in the fixation of phosphate ions, an effort was made to select for study relatively uniform materials, that is, materials in which one or another mineral group was predominant. Samples were fired at a variety of temperatures ranging from 20 °C to 1,000 °C (determined under identical conditions for each sample). Phosphorus uptake was measured using, on the one hand, phosphoric acid (Eber-

TABLE 1  
PHOSPHATE CONTENT OF POTS AND ADJACENT EARTH, BY LEVEL OF SAMPLING

SPECIMEN	LEVEL	AVERAGE PERCENTAGE PHOSPHATE		
		Earth Within Pot	Earth Immediately Surrounding	Pottery Body
Szob-Kiserdő, grave no. 19 <sup>a</sup> ; unused, no organic content	top	0.1032	—	0.1032
	middle	0.1032	0.1022	—
	bottom	0.1032	—	0.1032
Környe, grave no. 145 <sup>b</sup> ; used, no organic content	top	0.1108	—	0.2669
	middle	0.1121	—	—
	bottom	0.1121	—	0.4862
Kishomok, grave no. 49 <sup>c</sup> ; used, little organic content	top	0.1209	—	0.2745
	middle	0.1253	0.1284	0.5344
	bottom	0.1351	—	0.6372
Aszód, grave no. 45 <sup>d</sup> ; used, organic content	top	0.3375	—	—
	middle	0.3509	0.2521	0.2448
	bottom	0.3820	—	0.2761

<sup>a</sup> 10th century; excavated by K. Bakay in 1966.

<sup>b</sup> 6th century; excavated by I. Erdélyi and Á. Salamon in 1955.

<sup>c</sup> 6th century; excavated by I. Bóna in 1966.

<sup>d</sup> Late Neolithic, Lengyeli culture; excavated by N. Kalicz in 1966.

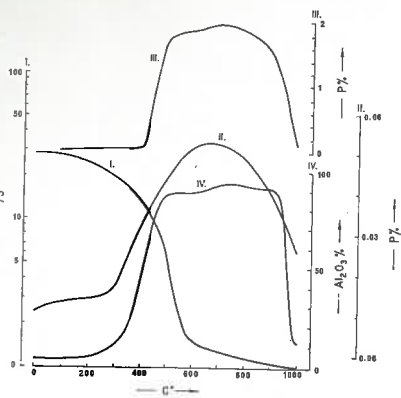


Fig. 6. Fired products of Zettlitz china clay at various temperatures of firing: (I) change in specific surface; (II) phosphorus uptake from aqueous solution of ATP; (III) phosphorus uptake from aqueous solution of phosphoric acid; (IV) acid solubility of alumina content.

hardt 1960), in view of its importance in the development of the phosphorus-bearing minerals and phosphates of the soil, and, on the other hand, adenosine triphosphate (ATP), an organic compound that yields phosphoric acid under experimental conditions and that occurs in relatively large amounts in various tissues.

All the fired clay products were tested for phosphate content before and after treatment with an aqueous solution containing phosphoric acid and/or ATP. The phosphorus uptake of fired products of china clay was found to increase considerably with firing temperature within a certain range, in association with the acid solubility of its alumina content and despite continuously decreasing specific surface (Fig. 6). The bonding of phosphate ions in fired products of china clay must be explained differently than the bonding observed in raw china clay (Coleman 1944, Black 1942, Hendriks and Dean 1947, Stout 1939). According to some authors (Keppler 1925, Neuman and Kobe 1926, Sokoloff 1912), the varying acid solubility of kaolinite (a hydrous silicate of aluminum that is the principal constituent of china clay) is related to water segregation, which accelerates transformation and disintegration of the structure of the mineral. Dehydrated kaolinite is chemically highly reactive (Budnikoff 1935, Tamman and Pape 1923), and so it might well be expected to enter more readily into reaction with phosphate ions than kaolinite in its natural state. If this were the case, one would expect to find aluminum phosphate in the fired clay product, but its presence has yet to be determined with certainty. Studies of the effects of phosphoric acid on various oxides (Bechtel and Ploss 1960, Budnikoff 1926,

Lehnhäuser 1954) have shown that it can form phosphates with alumina, calcium oxide, and other basic oxides.

The fired products of china clay and other materials containing kaolinite showed the greatest phosphorus uptake, but uptake was high in all potter's clays under these experimental conditions (see, for example, Fig. 7). In all clays tested, phosphorus uptake increased with temperature of firing up to 800°C and decreased gradually thereafter, regardless of decreasing specific surface and apparent porosity. It was greatest in products fired at 600–800°C—the very range of temperature at which pottery was probably fired under primitive conditions in ancient times.

#### SUMMARY

This report has been concerned with a possible new application to the materials of archaeology of known methods for measuring the phosphate content of the soil: the search for clues to the original use of a pot in the material of the pot itself. Previous attempts at determining use have dealt with the earth contents of the pot, and the results have suffered from the fact that to be reliable they must be obtained from a pot found in a known environment and containing undisturbed earth material. The approach here proposed is independent of the environment. It is based on the observation that the phosphate content of a given pot often varies regularly from top to bottom. The hypothesis is that phosphorus from the organic substance the pot once contained passes into the very porous material of the pot and through it into the surrounding earth. Study of a number of ancient unglazed pots and the earth within and surrounding them tends to support this view. The approach assumes that clays, even when fired, are able to bind phosphate ions permanently. Experiments designed to test this assumption show that such bonding does indeed occur in all clays as a function of firing temperature and that the ideal temperature for bonding is that at which pottery was probably fired in ancient times. Thus it appears that the measurement of the phosphate content of pots is likely to provide reliable evidence as to whether they once contained organic substances.

#### References Cited

- ARRHENIUS, O. 1931. Bodenanalyse in der Archäologie. *Zeitschrift für pflanzenernährung Düngung und Bodenkunde* 16:427–39.  
 ---. 1935. Markundersökning och Akeologie. *Formvänen* 30:565–76.  
 BECHTEL, H., and G. PLOSS. 1960. Über das Abbinden von keramischen Rohstoffe

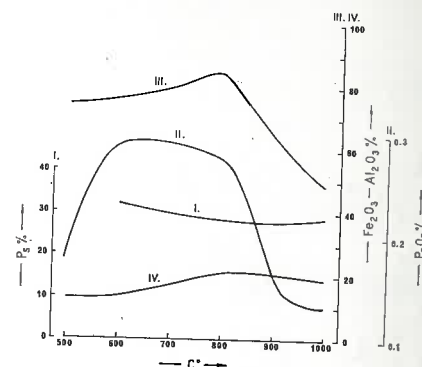


Fig. 7. Fired products of Mohács potter's clay at various temperatures of firing: (I) change in apparent porosity; (II) phosphorus uptake from aqueous solution of ATP; (III) acid solubility of alumina content; (IV) acid solubility of ferric oxide content.

mit monoaluminium-phosphat-Lösung. *Berichte der Deutschen Keramischen Gesellschaft* 37:362–67.

BLACK, C. A. 1942. Phosphate fixation by kaolinite and other clays as affected by phosphate concentration and time of contact. *Proceedings of the Soil Science Society of America* 7:123–33.

BLECK, R. D. 1965. Zur Durchführung der Phosphatmethode. *Ausgrabungen und Funde* 10:213–18.

BUDNIKOFF, P. P. 1926. Zur Frage der Erzeugung von in Wasser unzerwaschbaren Materialien aus rohem Ton. *Kolloid-Zeitschrift* 20:269–73.

---. 1935. Zur Untersuchung der Eigenschaften verschieden hoch erhitzten Kaolins. *Berichte der Deutschen Keramischen Gesellschaft* 16:349–54.

COLEMAN, R. 1944. The mechanism of phosphate fixation by montmorillonitic and kaolinitic clays. *Proceedings of the Soil Science Society of America* 9:72–78.

COOK, S. F., and R. F. HEIZER. 1965. Studies on the chemical analysis of archaeological sites. *University of California Publications in Anthropology* 2:1–102.

CORNWALL, I. W. 1958. *Soils for the archaeologist*. London: Phoenix House.

DAUNCY, K. D. M. 1952. Phosphate content of soils on archaeological sites. *Advancement of Science* 9:33–36.

DEAN, L. A. 1941. Fixation of soil phosphorus. *Advances in Agronomy* 1:391–411.

DUMA, G. 1968. Égetett anyagok foszforfelvétele (Phosphorus uptake of fired clays). *Építőanyag* 20:450–56.

---. 1969. Methode zum Feststellen der Bestimmung von urzeitlichen Gefässen. *Acta Archaeologica Hungarica* 21:359–72.

EBERHARDT, W. 1960. Die technische Weiterentwicklung der Vanadat-Molybat-Methode zur Schnellbestimmung der Phosphorsäure in pflanzlichen Substanzen. *Landwirtschaftliche Forschung* 13:303–7.

FELGENHAUER, F., and F. SAUTER. 1959. Phosphatanalytische Untersuchungen an paläolithischen Kulturgeschichten in Willendorf i.d. Wachau, N.Ö. *Archaeologica Austriaca* 25:25–34.

FRAUENDORF, E., and W. LORCH. 1940. Einfache Bodenuntersuchung im Dienste der Vorzeitforschung. *Nachrichtenblatt für Deutsche Vorzeit* 16:265–68.

GEIGER, H. 1936. Bodenuntersuchung und Archäologie. *Die Naturwissenschaften* 24:608.

- GRIMM, P. 1962. Phosphatuntersuchungen zur Besiedlung der Pfalz Tilled. *Ausgrabungen und Funde* 7:8-12.
- GUYAN, W. U. 1952. Beitrag zur topographischen Lokalisation einer Wüstung mit der Laktatmethode am Beispiel von Morgan. *Geographica Helvetica* 1:1-9.
- HALL, N. S., and A. J. MACKENZIE. 1947. Measurement of radioactive phosphorus. *Proceedings of the Soil Science Society of America* 12:101-6.
- HEM WALL, J. B. 1957. The fixation of phosphorus by soils. *Advances in Agronomy* 9:95-112.
- HENDRIKS, S. E., and L. A. DEAN. 1947. Basic concepts of soil and fertilizer studies with radioactive phosphorus. *Proceedings of the Soil Science Society of America* 12:98-100.
- JAKOB, H. 1951. Wüstungsforschung und Phosphatmethode I.-II. *Fränkische Blätter für Geschichtsforschung und Heimatspflege* 3:97-100, 101-4.
- . 1952. Über Ursachen anomaler Phosphatanreicherung auf Grabhügel. *Die Kunde* 3:37-40.
- . 1954. Zur Gebrauchsbestimmung von Grabhügelkeramik. *Forschungen und Fortschritte* 28:10-12.
- . 1955. Die Bedeutung der Phosphatmethode für die Urgeschichte und Bodenforschung. *Beiträge zur Frühgeschichte der Landwirtschaft* 2:67-85.
- JASMUND, K. 1951. Die silikatische Tonminerale. *Weinheim Monographien zu "Angewandte Chemie" und "Chemie-Ingenieur-Technik"* 60:47-49.
- KEPPLER, G. 1925. Zur Kenntnis der Tonsubstanz. *Sprechsaal* 58:614-15.
- LEHNHÄUSER, W. 1954. Feuerfeste Leichtsteine und Stampfmassen. *Euro-ceramic* 4:101-2.
- LENGYEL, I., and J. NEMESKÉRI. 1964. A csontvázleletek dekompozíciójáról (on the decomposition of skeletal finds). *Anthropologica Közlemények* 8:69-82.
- LORCH, W. 1939a. *Methodische Untersuchungen zur Wüstungsforschung*. Vol. 4. Jena: Gustav Fischer.
- . 1939b. Neue Methoden der Siedlungsgeschichte. *Geographische Zeitschrift* 45:294-305.
- . 1940. Die Siedlungsgeographische Phosphatmethode. *Die Naturwissenschaften* 28:633-40.
- . 1941a. Die Phosphatmethode im Dienste der Vorgeschichtsforschung. *Germanen Erbe* 6:55-59, 90-95.
- . 1941b. Chemische Spuren im Boden als Zeichen früherer menschlicher Besiedlung. *Die Umschau in Wissenschaft und Technik* 45:116-20.
- . 1943. Burgenforschungen mit der Phosphatmethode. *Die Umschau in Wissenschaft und Technik* 47:159.
- . 1944. Ergebnisse der Untersuchung württembergischer Burgberge mittels Phosphatmethode. *Die Naturwissenschaften* 32:99-100.
- . 1951. Die Entnahme von Bodenproben und ihre Einsendung zur Untersuchung mittels der siedlungs geschichtlichen Phosphatmethode. *Die Kunde* 2:21-23.
- . 1952. Das Erkennen des Relikt-Charakters von Waldkapellen aus dem Phosphatgehalt des Bodens. *Zeitschrift für württembergische Landesgeschichte* 11:246-53.
- MCALIFFE, C. D. 1947. Exchange reactions between phosphates and soils: Hydroxylic surfaces of soil minerals. *Proceedings of the Soil Science Society of America* 12:119-25.
- NEUMAN, B., and S. KOBE. 1926. Zur Kenntnis der Tonsubstanz. *Sprechsaal* 59:607-9.
- RAUTENBERG, E. 1934-35. Löslichkeit und Verteilung der Phosphorsäure im Boden. *Zeitschrift für Pflanzenernährung Düngung und Bodenkunde* 36:270-82.
- SAUTER, F. 1959. Phosphatanalytische Untersuchungen an dem Spät Latene-Haus aus Oberbergen, p.B. Krens, N.Ö. *Archaeologica Austriaca* 25:107-10.
- . 1967. Phosphatanalytische Untersuchung von Erdproben aus einem awarischen Grab. *Archaeologica Austriaca* 33:41-43.
- SCHMID, E. 1958. Höhlenforschung und Sedimentanalyse. *Schriften des Institutes für Ur- und Frühgeschichte der Schweiz* 13:21-36.
- SCHWARZ, G. T. 1967. Simplified chemical test for archaeological field work. *Archaeometry* 10:57-63.
- SOKOLOFF, A. M. 1912. Zur Frage des molekularen Zerfall des Kaolinitis im Anfangstadium des Glühens. *Tonindustrie Zeitung* 36:1107-10.
- SOLECKI, R. S. 1951. Notes on soil analysis and archaeology. *American Antiquity* 16:254-56.
- SPECHT, W. 1937. Chemische Abbaureaktionen bei der Leichenverzetzung III. *Ergebnisse der Allgemeinen Pathologie* 33:138-80.
- STEFANOVITS, P. 1963. *Magyarország talajai* (The Hungarian soil). Budapest: Akadémiai Kiadó.
- STOUT, P. R. 1939. Alternations in crystal structure of clay minerals as a result of phosphate fixation. *Proceedings of the Soil Science Society of America* 4:177-82.
- STOYE, K. 1950. Die Anwendung der Phosphatmethode auf einem mittelalterlichen Friedhof. *Jahresbericht für mitteldeutsche Vorgeschichte* 34:180-84.
- . 1955. Die Phosphatmethode in ihrer Anwendung auf die Grabung bei Wahlitz (Kreis Burg). *Beiträge zur Frühgeschichte der Landwirtschaft* 2:87-91.
- TAMMAN, G., and W. PAPE. 1923. Über den Wasserverlust des kaolins sein Verhalten im Festen Zustande zu den Carbonaten und Oxyden der Erdalkalien. *Zeitschrift für Anorganische Chemie* 127:43-67.
- UTESCHER, K. 1948. Das erdige phosphathaltige Sediment der Isenhöhle von Ranis. *Abhandlungen der Geologischen Gesellschaft, Berlin* 215:1-15.
- UZSÓKI, A. 1959. Előzetes jelentés a Mosonszentmiklós-Jánosházpusztai bronzkori temető asatának eredményeiről (Preliminary report on the results of excavations of the Mosonszentmiklós-Jánosházpuszta cemetery dating back to the Bronze Age). *Arrabona* 1:53-70.
- WALCHER, K. 1928. Studium über die Leichenfäulnis, mit besondere Berücksichtigung der Histologie derselben. *Wirkchows Archive* 268:17-30.

## Wanted

■ A suitable location for a controlled study of the effects on hearing of lifelong exposure to some steady loud noise. My research in the jungle area of southeast Sudan, in the Soviet Union, and elsewhere has shown that hearing loss in the aged is associated with the level of normal background noise. I now propose to study acuisis (sensitivity to sound) and blood cholesterol level in two groups from the same society, as homogeneous as possible, particularly in diet and stress, but differing in that one is exposed to constant noise—for instance, that of rapids, heavy surf, a waterfall, or a recurring geyser. A primitive society seems more likely to provide the desired homogeneity than a more advanced one, provided one is properly sensitive to the fact that, for example, fishing in dangerous waters may be more stressful than gathering coconuts. All the sites so far

proposed have proven unsuitable on investigation. For information leading to the selection of a place, I am offering a modest (\$100) prize. Please write: Samuel Rosen, M.D., 101 E. 73rd St., New York, N.Y. 10021, U.S.A.

■ Radiocarbon dates for early agricultural implements, grain samples, and the like, for a compilation being prepared by the editors of *Tools and Tillage* (see p. 57) in collaboration with the International Secretariat for Research on the History of Agricultural Implements and the Commission for Research on the History of Agricultural Implements and Field Structures (see CA 12:413). Please send information on the object and its provenience, radiocarbon number, date in the C<sup>14</sup> system and in years B.C. or A.D., a short note, if possible, on the treatment of the object, and references to previous publications or descriptions to the International Secretariat for

Research on the History of Agricultural Implements, National Museum, Brede, DK-2800 Lyngby, Denmark.

■ Information, to be incorporated into a report being prepared for CA, on demonstration materials for use in teaching physical anthropology and archeology—human and nonhuman primate skeletal materials, reproductions of fossil primate forms, reproductions of archeological artifacts, instruments, and slides and films. Besides the description of the item, I need as much information on the name and address of the supplier as possible, along with any note on how it may have special application. I am especially interested in sources of manufacture and supply outside of the United States. A copy of a preliminary article is available upon request to anyone interested in helping to amend it. Write: John M. Wilson, Anthropology and Sociology Department, Albion College, Albion, Mich. 49224, U.S.A.

