Title
DEDUCTION OF PROVENIENCE OF POTTERY FROM TRACE ELEMENT ANALYSIS

Permalink
https://escholarship.org/uc/item/5x2009f6

Authors
Perlman, I.
Asaro, Frank.

Publication Date
1967-10-01
DEDUCTION OF PROVENIENCE OF POTTERY FROM TRACE ELEMENT ANALYSIS

I. Perlman and Frank Asaro

October 1967

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Applications of Science to Medieval Archaeology
Los Angeles, California
October 26-28, 1967

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

DEDUCTION OF PROVENIENCE OF POTTERY FROM
TRACE ELEMENT ANALYSIS

I. Perlman and Frank Asaro

October 1967
The work reported here was undertaken on the premise that pottery clay from each area has a distinctive chemical composition. If this is so the ubiquitous ceramics of archaeology can be assigned places of origin independently of other characteristics such as style.

Others have had this thought; in particular, the elaborate study of Mycenaean and Minoan pottery by Catling, Richards and Blin-Stoyle (1) should be mentioned. These workers employed spectrographic analysis and concentrated on nine elements which include some of the minor constituents as well as such major elements as aluminum, calcium, magnesium and iron.

In the study to be reported here, we have used neutron activation analysis and have measured some 30 elements, but the approach is conceptually similar. In both studies pottery itself was analyzed with the objective of deriving internal correlations. This may be thought of as a classical archaeological approach which depends upon some distinctive uniformity within an area applying both to the geochemical history of the clay beds and to the treatment of raw materials by the potters. In a parallel but separate study which we have started, we are attempting to obtain information of another kind which should help in the interpretation of the first. The questions
which we hope to answer include (1) how uniform in composition is raw clay within a discrete clay bed and within an area of supposed geochemical uniformity, (2) what happens to the composition in preparing it for making pottery, (3) what happens during firing. This second approach is, in a sense, more fundamental but it is beset by a serious difficulty of a practical nature. There is a wealth of potsherds of known archaeological context but it is almost impossible to locate with certainty the clays from which they were made. The study can still be made using modern materials and from the results one can get some guidance in the interpretation of the ancient pottery. These problems in the diagnostic use of chemical makeup have been discussed by Shepard (2) in her critical review of the Catling, Richards and Blin-Stoyle paper.

It was mentioned that we used neutron activation analysis and obtained data on more than 30 elements. Attempts have been made in the past to use this technique on pottery (3) but the results seemed to be of limited value. The difference lies in the recent development of equipment for measuring gamma-ray spectra which is far superior to the best available at the time of the earlier studies. This dramatic change will be described further presently.

The basic constituents of pottery clays are hydrated aluminum silicates metamorphized in the weathering of certain igneous rocks. Within the basic aluminum silicate structure are found some minor constituents present to the order of a fraction of a percent to several percent. The raw clay used for pottery contains in addition to the clay minerals, residual components of the original rock and other materials which are picked up
during the transport of the clay by surface water. Conversely, secondary clay beds may be deficient in some of the components of the primary rocks because of settling during transport of the fine clay particles. Finally, tempering materials of one kind or another are deliberately added to the clay in order to obtain workable plasticity and to provide porosity and diminish shrinkage during firing.

Although the major constituents of pottery clay may well provide clues as to origin, results obtained through the years do not appear very encouraging. Attention was therefore addressed to the many trace elements which undoubtedly appear in any geochemical substance, clay included. The technique, in principle capable of satisfying this objective, is neutron activation analysis. Any element subjected to neutron irradiation has a finite (and fixed) probability of reacting with neutrons and at least one of the isotopes will be partially converted to a radioactive form. In principle, each radioactive specie is distinct from all others, and the measurement of the distinctive radioactivity can be related quantitatively to the abundance of the element in the specimen. As is true for any other scheme of analysis, neutron activation analysis does not measure all elements with equal sensitivity, and as a practical matter there are a sizeable number for which the method is not suitable. Nevertheless, where it can be applied it is capable of yielding considerable accuracy and, most importantly, a considerable number of elements can now be determined simultaneously. Before turning to how this is done on pottery, it is worth pointing out why neutron activation analysis is unique in its sensitivity to what we term "trace elements".

Speaking in general terms, the composition of rocks mirrors the composition
of the earth's crust, and elements which are rare in nature will be the trace elements of rocks. It is just these elements which react most readily with neutrons and hence are most sensitively detected. This fact has been used to account for the cosmic abundances of elements. At some stage in the genesis of elements they were subjected to huge numbers of neutrons; those which react readily were largely burned out converting to those which react slightly. For the purposes of our analysis of pottery, this is most fortunate because the radioactivity from the handful of major constituents will not completely mask that from the many trace elements. It will be seen that even with this fortuitous regulatory system the problems are severe enough.

The study reported here was conducted with archaeological materials, but the methodology rather than the possible archaeological significance will be stressed. A somewhat similar analysis has been made by Gordon et al. (4) on rock samples. From the start, we have received valuable guidance and encouragement from archaeologists Jay D. Frierman of U.C.L.A. and Robert Rodden from Berkeley. These colleagues also selected the sherds with careful attention to their archaeological context. They will of course play dominant roles in the analysis of the information in terms of its archaeological significance. Hopefully such papers will be ready for publication in the not-distant future.

II. NEUTRON ACTIVATION AND GAMMA-RAY SPECTROSCOPY

The measurements of the radiations from neutron-activated species can be explained most simply by an example, and the element iron has been selected. Iron as found in nature is made up of four stable isotopes. Only one of these, Fe$^{58}$, reacts with neutrons to give a radioactive isotope suitable for measurement. It turns out that Fe$^{58}$ only comprises 0.31% of iron, and its
probability for reacting with neutrons is not very high. The result is that iron is not detected with great sensitivity. This is a fortunate circumstance because pottery contains about 4% iron, and if it were strongly activated it might mask a number of the other elements. The product of neutron reaction is Fe\textsuperscript{59} which decays with a 45.6 day half-life and has a distinctive "spectrum".

Figure 1 shows a decay scheme for Fe\textsuperscript{59}. The diagram indicates that Fe\textsuperscript{59} decays to Co\textsuperscript{59} by $\beta^-$-emission and that only a very small percentage (0.3\%) of the decay events goes directly to the ground state of Co\textsuperscript{59}. Most of the decay events lead to several distinct excited states. The energies (in million electron volts) at which these lie above the ground state are indicated. Excited states such as these very quickly lose their energies by the emission of monoenergetic gamma rays. These are shown schematically by the vertical arrows. The energies are discrete as are the relative amounts to be observed, and these constitute the gamma spectrum for Fe\textsuperscript{59}.

The process and equipment for measuring the gamma-ray spectrum might be described as follows:

(1) Gamma rays impinge upon a "detector" which absorbs some of the photons converting the energy of each into an electrical pulse proportional to the photon energy.

(2) The electrical pulses are sorted electronically according to size and accumulated in a memory circuit.

(3) When a large number of events have accumulated the stored information can be read out.

Although not every photon enters the detector and not each one entering gives up its full energy, the system can be calibrated with standard
radioactive sources so that the data may be interpreted directly in absolute numbers of Fe\textsuperscript{59} atoms. A straightforward but tedious calculation tells one how much iron was in the specimen irradiated with neutrons.

Nothing has yet been said about how faithfully the detector responds to gamma-ray energy. Up to the present day almost all results reported on neutron activation analysis were based on measurements with the sodium iodide scintillation counter as the detector. Figure 2 displays the spectrum so obtained for Fe\textsuperscript{59}, and we see the five peaks corresponding to the five gamma-rays. The parts of the curve lying below the peaks are of considerable importance in gamma-ray spectrometry but will not be discussed here. If we focus attention on only the two prominent peaks at 1.095 and 1.292 MeV we see that they are quite well resolved, but the instrument gives a spread of energies for each rather than a monoenergetic spike. This is a limitation of the detector and is given quantitative expression by designating the width of the peak at the position of half of its maximum. In this case the peak widths are about 75 keV and the separation between the peaks is close to 200. Suppose now that we were not dealing with pure Fe\textsuperscript{59} but that the spectrum contained many other gamma-rays. We could only determine these accurately if each was separated by several peak widths from any other. Without further elaboration of this point one can say categorically that the sodium iodide detector is unsuitable for the analysis of a complex mixture of elements such as that in pottery.

Starting a very few years ago the semiconductor materials silicon and germanium have been developed as gamma-ray counters of superior resolution. Instead of a peak width of 75 keV, a good germanium counter can give
2 keV. The description of such counters and the attendant sophisticated electronics would take us rather far afield from our present purposes and will be omitted.\(^{(5)}\) It may, however, be instructive to show a part of the gamma-ray spectrum of irradiated pottery taken with each system. The section of the spectrum in Fig. 3 includes the two prominent gamma rays of Fe\(^{59}\) already discussed.

The lower scan of Fig. 3 was taken with our germanium system and covers about 20% of the energy range encompassed in a single measurement. The two peaks of Fe\(^{59}\) are of course still separated by 200 keV, but this separation is now about 80 times the peak width. It is seen that pottery also shows a number of other peaks some of which have been labeled and others unlabeled. The upper scan represents the identical measurement with a good sodium iodide system. For a mixture as complex as this, such spectra are quite unusable because of the relatively poor resolution. The undulations observed are the envelopes over the most prominent gamma rays. It may be mentioned in passing that the parts of the spectrum not shown here are much more congested with gamma-ray peaks.

III. ANALYSIS OF POTTERY

Neutron activation analysis may be applied to virtually any kind of material, but the optimum conditions are set on the basis of the radioactivities which are produced. The following prescription for analyzing pottery was arrived at by considering not only the nature of activated pottery but by the equipment at our disposal and, above all, by the requirement of automation to cope with the large number of analyses envisioned. In setting down this prescription it is hoped that the general outlines will be
intelligible to those who have never handled a problem such as this, but interspersed will be a number of vital details which will only be understood by those already familiar with equipment and concepts relevant to gamma-ray spectra.

A. Sample Preparation

The surface of the sherd was cleaned over an area of ~1 cm² using a sapphire scraper, and the remainder was masked with tape to avoid contamination from dust. A drill was fashioned from a rod of synthetic sapphire whose base could be placed in the chuck of an ordinary electric hand drill. The first portion of the powder drilled was discarded and then sufficient more powder removed to provide a sample of 100 mg. After showing on several specimens that no weight loss resulted from oven drying, this step was eliminated.

Approximately 100 mg of powder was weighed, mixed with 50 mg of cellulose and compacted into a pill using a hand-operated hydraulic press with stainless steel dies. The pills (1 cm X 1.5 mm) were wrapped in aluminum foil and packaged in an aluminum capsule for irradiation. Each batch contained in addition two pottery pills to which a measured amount of gold chloride has been added during the mixing stage to serve as the neutron flux monitor. The material was dried before pellets were pressed.

B. Irradiation And Measurement Schedule

Irradiations were carried out in the Triga Reactor in the University of California Department of Nuclear Engineering at a flux of approximately $8 \times 10^{13}$ neutrons/cm²·sec. The initial irradiation of each batch was carried out for 1 min in a plastic capsule, and gamma-ray analysis/started about 75 min
thereafter. Each pill was measured for 30 min except for those containing gold monitors for which 5 min counting was sufficient. This irradiation and measurement regime accentuated certain radioactivities with half-lives in the range of one to several hours and permitted the decay of those in the range of a few minutes. This choice eliminates the possibility of analyzing for aluminum and of obtaining (at best inaccurate) values for magnesium and vanadium.

The elemental analyses which are obtained in this campaign are dysprosium, manganese, sodium, and potassium. Samarium, strontium, and barium are also obtained, but better analyses for these elements result from the next stages.

The pills from the 1 min irradiation were repackaged and on a later day reirradiated for a period of 4 hours or, more recently, 8 hours. Because of the greatly extended irradiation time new monitors with considerably lower amounts of gold were used. These samples were analyzed for 50 min each after a cooling time of either 7 or 8 days. The principal reason for waiting one week is to permit the decay of the sodium radioactivity which is quite intense and diminishes the accuracy with which lesser components can be determined. This period of waiting, rather than a larger one, accentuates radioactivities with half-lives of the order of a few days. The elements obtained here are samarium, ytterbium, titanium, uranium, lanthanum, bromine, arsenic, calcium, and gold. Rather good numbers are also obtained for iron and scandium and less accurate numbers for cesium, antimony, and europium. However, all of these latter elements are better determined in the final stage.

The long-lived radioactivities are best determined by waiting until those mentioned above have diminished by decay. Consequently, after
a further delay of at least two weeks the same pills are again analyzed with a running time of about 6 hours for each. These measurements yield results for antimony, europium, iron, scandium, zinc, tantalum, cesium, nickel, zirconium, strontium, barium, hafnium, chromium, thorium, terbium, iridium, and cerium. In all, 33 elements are determined covering most of the periodic system and including almost all distinctive chemical types.

In separate irradiations, known quantities of all of the above elements were irradiated and measured under identical conditions. This standard procedure for activation analysis obviates the necessity for specifying neutron cross sections which may vary from reactor to reactor, and also removes the necessity for knowing gamma-ray abundances and counter efficiencies. The use of standard size samples eliminates uncertainties in the solid angle subtended by the detector. Finally, it is not necessary to know the neutron flux in the reactor as the gold monitors serve to normalize the different exposures. These will be mentioned further when the accuracies of the measurements are discussed.

Table 1 summarizes what has been said about the elements detected and gives further information useful to someone who wishes to do similar measurements. Also given is a set of results from a single piece of pottery to indicate typical abundance values. We must stress that an error as listed is not the true error but simply that part which comes from the statistics of radioactive counting. Those who are used to making such measurements will see reflected in these numbers the intensities of the photoelectron peaks measured and the relation of these intensities to the backgrounds under the peaks. In some cases, the indicated errors shown are a fraction of
Based upon independent measurements from duplicate samples and from the agreement of gold monitors we feel that it would be prudent to say that none of the abundances shown should be considered more accurate than 5 percent.* At the expense of considerable labor, errors should be reducible nearly to that of the statistical errors shown, but it is our judgment that this is not worthwhile. Although not proved, it is quite likely two pots which we would classify as identical because they were made at the same time from the same clay bed would vary in composition by several percent.

The validity of errors shown for those elements which have larger

*Evidence has accumulated over the course of this project which casts doubt on the comparability of "absolute" abundances obtained over a period of time within the errors mentioned here. Although the origin of this drift is not definitely understood we have enough built-in cross checks to permit corrections to be made. The nature of the problem is such that, whatever the cause, it can be eliminated by changing our method for monitoring the neutron flux. We propose to make up a "synthetic pottery" of known composition and to use samples of this for monitors in each irradiation in place of the gold pills. Each gamma-ray peak can then be compared with the corresponding peak in the specimens being analyzed. This system will involve minor changes in data processing but will eliminate errors introduced by shifts in neutron energy distributions and shifts in behavior of the analyzing equipment.
uncertainties are also in question but for other reasons. A large statistical error implies in most cases that the peak height is small compared with the background. Suppose that the peak intensity is 1,000 counts above a background of 20,000 counts. This measurement has a statistical error of ±20%. The background is the envelope of Compton distributions of all gamma-rays and can change slightly in height and shape depending upon variations of the constituents. If at the place we choose for background subtraction there has been a shift of only 1%, this would introduce an additional 20% error in our analysis. As experience is gained it will be possible to learn how to handle the background problems more judiciously and such refinements would indeed be worth the effort because the work only need be done once for all measurements.

C. Data Accumulation And Processing

Gamma-ray spectra are taken by recording the number of pulses corresponding to a certain small energy interval in a storage unit called a channel. The instrument used for the present study contains 1,600 channels. The lower limit of pulse heights accepted and the pulse amplification can be fixed; in this case the lowest energy accepted was 50 keV and the upper limit 1700 keV. Accordingly, the energy interval per channel was slightly greater than one kilovolt. The detector employed was a germanium counter of approximately 5 cm³ volume. The detector with its attendant electronics produced gamma-ray peak widths of about 2.5 keV for the higher energy gamma-rays.

In measurements such as these there will be low-intensity peaks of value as well as strong peaks, so in order to accumulate statistically valid numbers of counts it is desirable to count samples which are highly radioactive.
The stronger a sample is the more "coincidences" occur, a term relating to a pulse starting through amplifier and analyzer before recovery from the previous pulse. Such pile-up pulses must be rejected as much as possible because they broaden peak widths and diminish the accuracy of the measurements.

Technical points concerning this matter are the following: The irradiation schedule outlined above was geared to produce sample strengths of less than 7,000 counts per second. In general, the corresponding "dead time" of the instrument was 25% or less. The dead time and the count rate were recorded for each measurement, and a small correction factor (determined empirically) was applied to the peak intensities. The separate application of this correction is a necessity of the manner in which the data are processed.

The processing of the data starts with the emptying of the data storage unit onto magnetic tape. This reproduces all of the information stored in the 1,600 channels in form suitable for computer analysis. The analyzer was stabilized automatically by a digital threshold stabilizer which effectively held a preselected peak dead-center on a particular pair of channels. This stabilization means that from measurement to measurement the positions of the various peaks will not drift significantly, and the computer may be instructed to add specific channel data to obtain the peak intensities. Instructions are also given as to which channels are to be used for subtraction of the background for each peak. Different ways of handling the background subtraction arise from the detailed shape of the curve in the vicinity of a peak and the presence or absence of other peaks nearby. A number of background "options" evolved and the use of these became a part of the computer program and instructions. The dead time correction mentioned
above rises in part from the fact that at large dead times the peaks are
broadened somewhat and some of the stored counts will appear in channels
outside of those which the computer is instructed to add. For a few elements,
the best peak for analysis contained some counts from the tail of nearby peaks.
The amount of this tailing depends upon the amount of the element producing
the interfering peak. The computer program also included the calculation of
how much was to be subtracted from the final abundance of the element in
terms of the abundance of the interfering element.

In addition to the determination of the numbers of counts (peak
intensities) for each of the peaks analyzed, the computer program included
the calculations all the way to the final print out of the abundance of each
element in the pottery. Those familiar with these simple but tedious com-
putations will recognize the involvement of the following factors: integrated
neutron flux, abundance and cross section of the stable isotope which be-
comes transmuted, abundance of the specific gamma ray from each radioactive
isotope, geometry factor and counting efficiency for the detector, and decay
correction for the activated specie. Although all of these factors are
implicit in any determination, some are handled indirectly by use of stan-
dards consisting of known amounts of the elements. For example, there is
within the calculation a product of the neutron cross section, gamma-ray
abundance and counting efficiency of the gamma ray—all constants for a parti-
cular gamma-ray and analyzer assembly. In comparing with a standard, any
two of these may be fixed arbitrarily and the "errors" so incurred absorbed
in the third factor. Since other workers would follow similar procedures,
the ultimate analytical results should be strictly comparable even though
(for example) the cross sections employed are different.

Although we have analyzed over 250 sherds at the present writing, the standardization process was deferred and is not yet in final form. The examples of analyses to be given are therefore unfortunately not absolute values. Some of the constants which we shall determine by means of the standards were taken from the literature, and these can be at variance from what we shall determine. For illustration, the values given for the element lanthanum will not change relative to each other, but the absolute values will have to be revised. By the same token inferences on the relative amounts of different elements will have to be deferred. Only when meaningful absolute values can be put down will it be possible to compare our analyses with those done in other laboratories.

IV. STATEMENT OF THE ARCHAEOLOGICAL PROBLEM

Before looking at some actual analyses, it may be well to set down the presently conceived limitations on what the analyses could possibly show. First, a few words should be said about the geochemical basis for judging provenience of pottery. Considering the complexity of the parent rocks and the sensitive fractionation possible in the formation of clay beds, it is possible that no two sources of pottery clay will prove to be the same if a large number of elements are compared. If so, then even a single source of pottery clay may prove to be inhomogeneous. We can only conjecture about this point at present because nothing has yet been done to explore such variations. The reasons for temporarily ignoring this problem are very much the same as those stated by Catling, Richards and Blin-Stoyle. (1) They, as we, confined their attention to the finished pottery because it may be no
simple matter to relate pottery directly to clay beds. In most instances it might be quite difficult to satisfy one's self that he is actually sampling the sources from which the ancient potters drew their materials. Further, one cannot be sure how they processed the raw clay, removing some materials and adding others. There need be less uncertainty concerning the problem of what happens to the composition during the process of firing because this matter could be explored by experiment. Despite the complexities envisioned, the prospects of getting meaningful information are by no means hopeless. As an example, some conclusions may be drawn on uniformity to be expected within a clay bed by simply sampling and ignoring pottery association.

For the time being we are therefore relying upon the traditional approach in archaeology, that is, the development of internal correlations to establish the norm for uniformity. Superimposed upon this is the desirability of any external cross checks which can be elicited. All in all, this calls for a rather lengthy development in which the boundaries of reliability are set by an accumulative process rather than a definitive settlement at one time.

One other point should be mentioned which is perhaps unique to the type of analysis under discussion. Much of the information obtained concerns trace elements present in the parts-per-million range. The inadvertent contamination of our specimens is a real problem and must be guarded against. For example, antimony found to the extent of 1 ppm corresponds to an amount of only 0.1 microgram in a 100 mg. sample. If we employ normal diligence, experience has shown that abnormal values do not occur very often, but they do occur. Where such cases occur, an independent
sample should be run. A more difficult problem, and a more interesting one, is the possibility of contamination at the source. There is abundant evidence that ancient peoples used a variety of substances in concentrated state: ores for metallurgy, pigments for decorating, cosmetics, materials for glass—to name a few. It is quite conceivable that pottery would be contaminated significantly particularly when a rich source of an element corresponds with a trace element in the pottery clay. Evidence for this type of contamination may be difficult to single out unless incidents are repetitive, but where it is obtained one has information of archaeological value.

V. RESULTS

Some representative analytical results are presented in histogram form in Figs. 4 - 8. It should be borne in mind in viewing these that the variations in content for a particular element from a particular site cannot be attributed to lack of precision in measurement. Some of the factors which could cause such variations in pottery composition have already been mentioned. In selecting data for these figures, some have been included specifically to illustrate these points. However, each set shown is complete in the sense that no pieces of the type selected have been left out. For example, all of our measurements of the red-ware and black-topped ware from Nag' ed-Deir have been included.

The particular elements chosen for illustration represent only about one-fourth of those for which we have data. Among those omitted are some, such as arsenic, which seem to be rather chaotic, and others which represent some of the more prominent constituents of clay. However, some 15 elements not shown are probably as useful diagnostically as the eight
A brief description of the material examined follows:

(1) "Nag' ed-Deir" refers to a predynastic cemetery in Upper Egypt and materials are from the large Reisner Collection in Berkeley. The selection of representative sherds was made by Robert Rodden. Typologically the sherds fell into several groups.

(a) "Red-ware" (r.w.) or "plum-ware" is characterized by a fairly course texture and a heavily burnished slip of high iron content.

(b) "Black-topped ware" (b.t.) is similar in composition to the red-ware, and the data for these types have been combined.

(c) Decorated ware (dec.) refers to contemporaneous pottery with a hard pink body decorated with red pigment.

(d) "Wavy-handled ware" (w.h.) are all of the early type in which the handles are pronounced. In later evolutionary states this handle degenerated into a decorative motif. In large part, the compositions of these specimens were the same as for the decorated ware and were so combined.

(2) "Sialk" refers to the site in northern Iran which had a long occupation period stretching from 6000 B. C. to 1000 A. D. Materials representative of most of the strata were selected by Jay Frierman and in due course all the analytical results will be presented along with the inferences of archaeological value. For the present purposes we are showing only combined pieces from levels III 6 and III 7 which are often typologically indistinguishable.

(3) "Al 'Ubaid" is a site of southern Babylonia slightly inland from the Euphrates River, and our sherds are of approximate date 4000 B. C. These
materials came from the Collection at U.C.L.A. and were obtained by Dr. Frierman.

(4) "Mycenae" is too well known to require description. The few pieces so far analyzed were obtained for us by Dr. Frierman and not all are of known provenience.

(5) In Fig. 8 will be presented some data taken from sherds excavated by Dr. Dothan at "Tell Ashdod" in the southern coastal region of Israel. These also were obtained by Dr. Frierman. Ashdod was a Philistine city of about 1400 B.C. and the few sherds analyzed fell distinctively into three typological groups: (a) Philistine local, (b) Cypriot imports, (c) Mycenaean imports.

In examining the data of Figs. 4-7 it should be borne in mind that the present stage of this study is not aimed at settling any archaeological problem. Materials were selected whose origins are surmised to be correct and which are typologically distinctive. Whether or not some of the spread in values will ultimately prove to be an unplanned-for excursion into archaeology we do not know.

First, a mere glance at the Nag' ed-Deir material shows that the two categories which can be easily distinguished by visual examination are also quite different in composition. We wish to point out, however, that we already have abundant evidence that such clear correlations are not universal. From sites neighboring on Nag' ed-Deir in Upper Egypt we have typologically similar specimens which are significantly different in composition and we have found the intrusion (inadvertent) of a sherd in the Sialk collection which has not been previously described but which definitely "belongs" to Sialk in
its chemical make up. Reiterating, it is not our purpose here to pursue such leads of archaeological interest. Only one further point will be mentioned and this relates to the few sherds designated "Mycenae". Of these, three were excavated at Mycenae and two (cross-hatched in the figures) were found on Kea.

Returning to the data, it is seen that Nag' ed-Deir red-ware is the lowest of all in cesium and quite low in thorium. On the other hand, this particular pottery is the highest of all in some other elements not shown here. Sialk and Ubaid overlap in hafnium and lanthanum, are somewhat different in uranium and thorium, and are distinctly different in nickel, chromium and cesium. Mycenae and Sialk are both high in cesium but are distinctly different in nickel and chromium. Gross comparisons of this nature can be continued by the reader and, as already mentioned, could be done with many other elements not shown here. The objective, however, is to pursue this matter in much greater detail by applying it to materials which are typologically indistinguishable or which have not been "typed" with certainty at all.

In Fig. 8 we have analytical results on 6 elements for three types of sherds found at Tell Ashdod. This is a rather remarkable set in that there is virtually no overlap between any of the three types for any of the elements. There were only 2 sherds of Mycenaean type. The third, presented as a cross-hatched marker, was selected arbitrarily from a small group excavated at Mycenae. Examination of the other data (not shown here) produced 15 other elements which had similar differences not including elements which generally vary coherently with those selected. For example, these 15 elements did not include any rare earth elements because this type is already represented by lanthanum.
ACKNOWLEDGEMENTS

We wish to thank again Drs. R. Rodden and J. F. Frierman for their invaluable participation in this study and for the use here of some of the results before the more complete exposition in archaeological context. We are also indebted to our assistants Mrs. Helen V. Michel and Miss Susanne Halvorsen for their skilled and painstaking efforts in almost all phases of this work. This study would not have been possible without the contribution of Mr. Duane Mosier in setting up the electronic pulse-height analyzer and the interface equipment which permitted computer processing of the data. We are also indebted to Professor Lawrence Ruby and Dr. Leonel Stollar of the University of California Department of Nuclear Engineering for the many carefully controlled irradiations in the Berkeley Research Reactor.

This work was performed under the auspices of the U. S. Atomic Energy Commission.
REFERENCES


5. For a popular account of semiconductor counters and their applications, see J. M. Hollander and I. Perlman, Science 154, 3745 (1966).
<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope Examined</th>
<th>Half Life (keV)</th>
<th>y-ray Abundance in pottery</th>
<th>Statistical error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy</td>
<td>$^{165}$ Dy</td>
<td>2.3h</td>
<td>1.94 x 10^{-6}</td>
<td>0.05 x 10^{-6}</td>
</tr>
<tr>
<td>Mn</td>
<td>$^{56}$ Mn</td>
<td>2.6h</td>
<td>4.84 x 10^{-4}</td>
<td>0.16 x 10^{-4}</td>
</tr>
<tr>
<td>Na</td>
<td>$^{24}$ Na</td>
<td>15.0h</td>
<td>1.02 x 10^{-2}</td>
<td>0.005 x 10^{-2}</td>
</tr>
<tr>
<td>X</td>
<td>$^{42}$ X</td>
<td>12.4h</td>
<td>2.0 x 10^{-2}</td>
<td>0.18 x 10^{-2}</td>
</tr>
<tr>
<td>Sr</td>
<td>$^{87}$ Sr</td>
<td>2.8h</td>
<td>3.1 x 10^{-4}</td>
<td>0.4 x 10^{-4}</td>
</tr>
<tr>
<td>Sm</td>
<td>$^{153}$ Sm</td>
<td>1.9h</td>
<td>4.92 x 10^{-6}</td>
<td>0.01 x 10^{-6}</td>
</tr>
<tr>
<td>Ti</td>
<td>$^{47}$ Ti</td>
<td>3.4a</td>
<td>3.06 x 10^{-3}</td>
<td>0.09 x 10^{-3}</td>
</tr>
<tr>
<td>Lu</td>
<td>$^{177}$ Lu</td>
<td>5.7a</td>
<td>7.4 x 10^{-7}</td>
<td>0.1 x 10^{-7}</td>
</tr>
<tr>
<td>Yb</td>
<td>$^{175}$ Yb</td>
<td>4.2a</td>
<td>2.88 x 10^{-7}</td>
<td>0.08 x 10^{-7}</td>
</tr>
<tr>
<td>U</td>
<td>$^{239}$ U</td>
<td>2.3a</td>
<td>1.12 x 10^{-5}</td>
<td>0.03 x 10^{-5}</td>
</tr>
<tr>
<td>La</td>
<td>$^{140}$ La</td>
<td>1.7d</td>
<td>1.56 x 10^{-5}</td>
<td>0.01 x 10^{-5}</td>
</tr>
<tr>
<td>Br</td>
<td>$^{82}$ Br</td>
<td>1.5d</td>
<td>3.4 x 10^{-6}</td>
<td>0.3 x 10^{-6}</td>
</tr>
<tr>
<td>As</td>
<td>$^{75}$ As</td>
<td>1.1d</td>
<td>8.7 x 10^{-6}</td>
<td>0.4 x 10^{-6}</td>
</tr>
<tr>
<td>Ca</td>
<td>$^{47}$ Ca</td>
<td>4.5d</td>
<td>1.31 x 10^{-1}</td>
<td>0.06 x 10^{-1}</td>
</tr>
<tr>
<td>Au</td>
<td>$^{198}$ Au</td>
<td>2.7d</td>
<td>1.9 x 10^{-8}</td>
<td>0.15 x 10^{-8}</td>
</tr>
<tr>
<td>Sb</td>
<td>$^{124}$ Sb</td>
<td>60h</td>
<td>2.1 x 10^{-6}</td>
<td>0.1 x 10^{-6}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope Examined</th>
<th>Half Life (keV)</th>
<th>y-ray Abundance in pottery</th>
<th>Statistical error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>$^{152}$ Eu</td>
<td>12.7y</td>
<td>1408</td>
<td>5.1 x 10^{-7}</td>
</tr>
<tr>
<td>Co</td>
<td>$^{59}$ Co</td>
<td>5.3y</td>
<td>1332</td>
<td>1.25 x 10^{-5}</td>
</tr>
<tr>
<td>Fe</td>
<td>$^{59}$ Fe</td>
<td>4.6d</td>
<td>1292</td>
<td>3.35 x 10^{-2}</td>
</tr>
<tr>
<td>Sc</td>
<td>$^{46}$ Sc</td>
<td>8.4d</td>
<td>1280</td>
<td>1.21 x 10^{-5}</td>
</tr>
<tr>
<td>Rb</td>
<td>$^{86}$ Rb</td>
<td>193</td>
<td>1077</td>
<td>6.4 x 10^{-5}</td>
</tr>
<tr>
<td>Ta</td>
<td>$^{182}$ Ta</td>
<td>115d</td>
<td>1222</td>
<td>1.25 x 10^{-6}</td>
</tr>
<tr>
<td>Cs</td>
<td>$^{131}$ Cs</td>
<td>2.0y</td>
<td>796</td>
<td>7.4 x 10^{-6}</td>
</tr>
<tr>
<td>Ni</td>
<td>$^{58}$ Ni</td>
<td>71d</td>
<td>810</td>
<td>9.4 x 10^{-5}</td>
</tr>
<tr>
<td>Zr</td>
<td>$^{95}$ Zr</td>
<td>66d</td>
<td>756 &amp; 783</td>
<td>1.5 x 10^{-4}</td>
</tr>
<tr>
<td>Ba</td>
<td>$^{131}$ Ba</td>
<td>12.0d</td>
<td>496</td>
<td>4.1 x 10^{-4}</td>
</tr>
<tr>
<td>Hf</td>
<td>$^{181}$ Hf</td>
<td>42d</td>
<td>482</td>
<td>2.96 x 10^{-6}</td>
</tr>
<tr>
<td>Cr</td>
<td>$^{51}$ Cr</td>
<td>28d</td>
<td>320</td>
<td>1.35 x 10^{-4}</td>
</tr>
<tr>
<td>Th</td>
<td>$^{233}$ Th</td>
<td>27d</td>
<td>312</td>
<td>8.45 x 10^{-6}</td>
</tr>
<tr>
<td>Tb</td>
<td>$^{160}$ Tb</td>
<td>72d</td>
<td>298</td>
<td>2.9 x 10^{-7}</td>
</tr>
<tr>
<td>Ce</td>
<td>$^{141}$ Ce</td>
<td>32d</td>
<td>135</td>
<td>1.9 x 10^{-5}</td>
</tr>
<tr>
<td>Ir</td>
<td>$^{192}$ Ir</td>
<td>74d</td>
<td>316</td>
<td>&lt;5 x 10^{-10}</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1 Decay Scheme of Fe\textsuperscript{59}

Fig. 2 Gamma ray spectrum of Fe\textsuperscript{59} taken with a sodium iodide counter

Fig. 3 Partial gamma ray spectra of pottery. Top curve-spectrum taken with good NaI detector, lower curve-spectrum taken with good Ge detector.

Fig. 4 Cesium and uranium composition of pottery excavated from various sites. Cross hatched data represents pottery excavated at Kea.

Fig. 5 Thorium and chromium composition of pottery excavated from various sites. Cross hatched data represents pottery excavated at Kea.

Fig. 6 Cobalt and lanthanum composition of pottery excavated from various sites. Cross hatched data represents pottery excavated at Kea.

Fig. 7 Nickel and hafnium composition of pottery excavated from various sites. Cross hatched data represents pottery excavated at Kea.

Fig. 8 Partial composition of pottery excavated at Tell Ashdod. Cross hatched data represents sherds excavated at Mycenae.
45 day Fe$^{59}$
3" $\times$ 3" - 2 No 1
3-21-62
ABSORBER 1.18g/cm² Be
SOURCE DIST 10 cm (c)
ENERGY SCALE 1 KeV PHU(Ce)

PULSE HEIGHT

0.091
0.145
0.337
1.097
1.269

XBL 6711-6078
Partial gamma ray spectra of pottery

Gammar ray energy (keV)

Gamma ray intensity

Fig. 3
Fig. 4
<table>
<thead>
<tr>
<th>FREQUENCY OF OCCURRENCE</th>
<th>THORIUM</th>
<th>CHROMIUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mycenae</td>
<td><img src="image1" alt="Bar Graph" /></td>
<td><img src="image2" alt="Bar Graph" /></td>
</tr>
<tr>
<td>Al- 'Ubaid</td>
<td><img src="image3" alt="Bar Graph" /></td>
<td><img src="image4" alt="Bar Graph" /></td>
</tr>
<tr>
<td>Sialk III 6 and 7</td>
<td><img src="image5" alt="Bar Graph" /></td>
<td><img src="image6" alt="Bar Graph" /></td>
</tr>
<tr>
<td>Nag' ed - Deir (w.h. and dec.)</td>
<td><img src="image7" alt="Bar Graph" /></td>
<td><img src="image8" alt="Bar Graph" /></td>
</tr>
<tr>
<td>Nag' ed - Deir (r.w. and b.t.)</td>
<td><img src="image9" alt="Bar Graph" /></td>
<td><img src="image10" alt="Bar Graph" /></td>
</tr>
</tbody>
</table>

**Fig. 5**
<table>
<thead>
<tr>
<th>FREQUENCY OF OCCURRENCE</th>
<th>COBALT</th>
<th>LANTHANUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mycenae</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-'Ubaid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sialk III 6 and 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nag'ed-Deir (w.h. and dec.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nag'ed-Deir (r.w. and b.t.)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**ABUNDANCE IN POTTERY (ppm)**

Fig. 6
<table>
<thead>
<tr>
<th>FREQUENCY OF OCCURRENCE</th>
<th>NICKEL</th>
<th>HAFNIUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mycenae</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al- 'Ubaid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sialk III 6 and 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nag'ed-Deir (w.h. and dec.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nag'ed-Deir (r.w. and b.t.)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RELATIVE ABUNDANCE IN POTTERY</th>
<th>ABUNDANCE IN POTTERY (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 40 60 80 100</td>
<td>4 6 8 10</td>
</tr>
</tbody>
</table>

Fig. 7
SHERDS FROM TELL ASHDOD

<table>
<thead>
<tr>
<th></th>
<th>SCANDIUM</th>
<th>LANTHANUM</th>
<th>CESIUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mycenaean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cypriot</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Philistine</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FREQUENCY OF OCCURRENCE

<table>
<thead>
<tr>
<th></th>
<th>IRON (%)</th>
<th>SAMARIUM</th>
<th>THORIUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mycenaean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cypriot</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Philistine</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ABUNDANCE IN POTTERY (ppm)

Fig. 8
This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.