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Neutron activation analysis of archaeological artefacts

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The elemental compositions of archaeological artefacts, ancient and medieval coins, and metallic art objects have been determined by non-destructive neutron activation analysis. Examples are given of studies of prehistoric trade routes and cultural contacts based on the identification of the geologic origins of obsidian artefacts, of early economic systems based on the determination of debasement patterns in medieval Islamic and Western gold and silver coinage, the region of manufacture as well as authentication of ancient metallic art objects based on trace element analysis. Special procedures devised for performing these analyses are described.

Introduction

There are a number of reasons why neutron activation analysis is particularly useful in the examination of archaeological artefacts. Because of the high sensitivity of detection of many of the elements, only minute samples are needed; if the object being studied is particularly valuable, reliable analyses can be performed using less than a milligramme of material. In other cases, the whole object can be subjected directly to analysis since non-destructive analyses can be performed. This latter feature is particularly useful in the analysis of coins. Using modern instrumentation, it is possible to automate some of the analysis procedures. Such automation is almost a requirement in cases where it is desirable to analyse hundreds or thousands of samples in order to obtain sufficient data to solve a problem.

A typical analysis procedure is relatively simple. A group of samples and chemical standards of known composition are placed in a nuclear reactor and irradiated with thermal-energy neutrons. Generally, less than one nucleus in every 10^8 is converted into a radioactive nucleus. Some of the radioisotopes so produced have half lives too short to permit detection unless special rapid analysis methods are used. A few radioisotopes, upon decay, will either not emit γ rays or emit γ rays too weak to detect easily. In some cases another stable isotope of the element will be produced. As a result of these considerations it will be difficult or even impossible to detect certain elements when using thermal neutron activation followed by analysis of the γ rays emitted by the irradiated sample. However, this usually is a minor hindrance and may even be desirable to some extent. The elements that are not easily detected tend to be those at the beginning of the periodic table and include the common elements: hydrogen, oxygen, nitrogen, carbon, and silicon. Usually knowledge of the content of these elements in an artefact provides very little information of use in solving problems of interest to archaeologists. It is the elements present in small, even minor amounts at the parts-per-million levels that are often the most informative. Given in table 1 are typical levels of detection sensitivity for neutron activation analysis. The factors that determine the ordering in this table are nuclear in origin: the probability that a given type of nucleus will absorb neutrons, and the half life for radioactive decay.

Following the irradiation of a set of samples and chemical standards it is only necessary to determine the types of γ rays emitted by the sample. Since each radioisotope emits γ rays is shown in figure 2. Various obsidian projectile points as well as obsidian flakes have been found in the 2000-year-old Hopewell Indian burial mounds located principally in the states of Ohio, Indiana and Illinois. Although the first obsidian was recovered from these mounds over 120 years ago, and anthropologists had speculated as to the origin of the obsidian, it was not until the present analyses were performed that it was possible to identify the sources. Two types of obsidian were found. The first was matched with the composition of that from Obsidian Cliff and corresponds to the horizontal set of data at 1.0 in figure 2. The second type, whose composition is given by closed circles in figure 2, corresponds in composition to another source of obsidian also located in Yellowstone National Park; data for this second source are given by squares in figure 2. Thus, there had existed in North America, 2000 years ago, contact that extended over 2400 km.

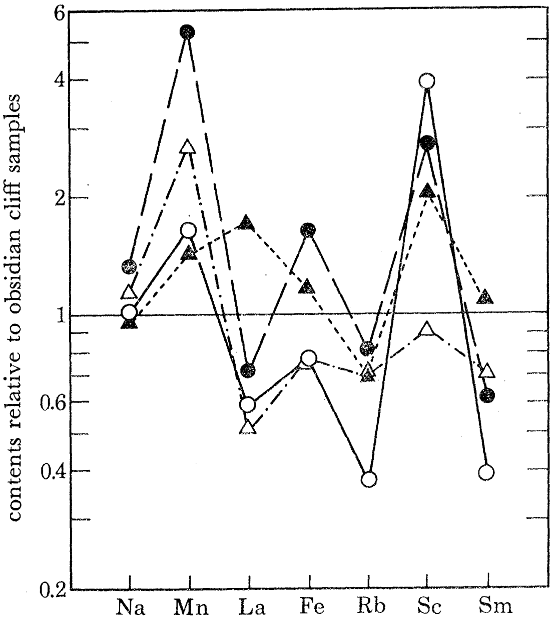

FIGURE 1

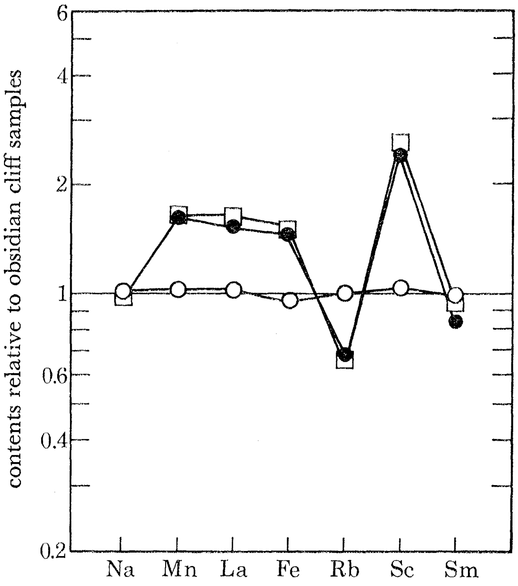

FIGURE 2

FIGURE 1. Composition of four obsidian sources relative to that of Obsidian Cliff, Yellowstone National Park. Glass Butte, Ore, ○; Cerro de la Nevejas, Mexico, ●; Vias Mountain, New Mexico, △; Powder River, Montana, ▲.

FIGURE 2. Composition of obsidian samples relative to that of Obsidian Cliff, Yellowstone National Park. Archaeological obsidian artefacts from Hopewell Indian burial mounds ○ and ●. Another geologic source in Yellowstone National Park □.

Similar analyses of prehistoric Near Eastern obsidian artefacts from sites in Syria and Iraq that date to 7500 to 3500 B.C. have been shown to correspond to a geologic obsidian source located principally in the Lake Van region.

As noted earlier, analyses of this type are not limited to obsidian. At The University of Michigan an extensive programme is under way involving analyses of flint, chert, chalcedony, jasper, quartzite, ilmenite, haematite, and magnetite. All of these substances exhibit within single geologic sources much more variability in composition than does obsidian. Hence, it is necessary to determine the composition of many more elements in order to match samples and sources. Preliminary data indicate that such matching will, to some extent, be possible.

Silver coin analysis

Although we now progress to objects that belong to the historic period, it should be emphasized that studies of certain cultures, such as those in the Near East and Middle East from about 500 B.C. to A.D. 800, are dependent to a large extent on the examination of coins and metallic art objects found in archaeological excavations. In the past, these examinations have generally been limited to a visual analysis of the objects. For coins especially it is important to know their metallic content for this will provide information of use in suggesting the types of economic pressures which existed.

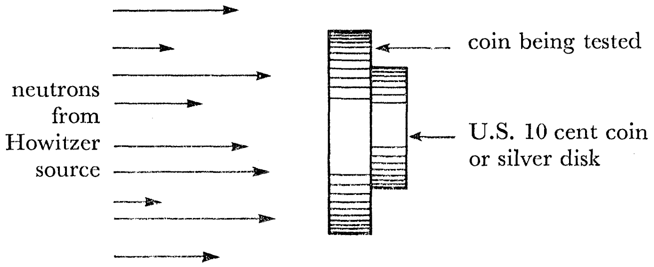

Figure 3. Method of neutron irradiation of coins using a Pu–Be neutron Howitzer source.

At The University of Michigan there was developed a rapid, non-destructive neutron activation analysis method for silver in coins (Gordus 1968*b*). It involves irradiating a coin and a silver disk taped to the coin, figure 3, for 1 min in a low-intensity neutron flux of 10^4 cm^{-2} s^{-1}. The neutrons are produced in a plutonium–beryllium mixture by a secondary nuclear reaction which occurs when the plutonium decays. Such Pu–Be sources are small and portable. Because of the low neutron intensity only 24 s half life ^{110}Ag and 2.4 min half life ^{108}Ag isotopes are produced in sufficient quantity to be detected. The short half lives of these isotopes result in almost all of the induced activity being completely decayed in 10 to 15 min. The coins are unharmed and there is no residual radioactivity.

It was necessary to modify the usual irradiation procedure by taping a silver disk to the coin being irradiated in order to obtain data to correct for neutron-absorption effects in the coin. These effects are strongly dependent on the coin thickness as seen in figure 4, where data are given for coins of known silver content. By dividing these same data by the activity produced in the silver disks it was found that thickness-independent values were obtained for most coins. as seen in figure 5.

The analysis procedure, therefore, involves irradiating a series of modern coins of known silver content to obtain an average value for the constant: (counts in coin) × (counts in disk)$^{-1}$ × (g coin)$^{-1}$ × (percentage silver in coin)$^{-1}$. In analysing a coin of unknown silver content this constant is used and the percentage silver calculated from the equation for the constant.

Over 3500 coins have been analysed using this method; generally 8 to 10 repeat analyses were performed in order to obtain a more statistically reliable silver content, the average of these analyses being valid to about ±1.5 %

A typical set of data are shown in figure 6 where there are plotted the silver contents for over 350 Sasanian dirhems. Some periods of marked debasement are seen for this pre-Islamic dynasty, the most pronounced being during the reign of Shapur I. This Sasanian king was involved in various wars against Roman armies. A number of possible reasons can be advanced to explain why he would have debased his coinage. Economic pressures due to increased expenses

Although it would be possible to determine the exact mass of the streak and thus obtain quantitative analytical data, the mass analysis procedure would be too lengthy and in fact probably unnecessary. If coins are debased, invariably this is accomplished by adding copper. Lead is not detected in this analysis and chemical analyses of ancient and medieval coins have shown that the amount of lead and other impurities is generally less than 1 or 2 %. Gold is an impurity associated almost entirely with the silver as is shown by the fact that almost no gold is found in copper coins. The gold contents of ancient silver coins are usually less than 1 % and apparently its presence was unknown to the ancient minters. Further, as our data show, the gold content of the silver provides a means of distinguishing between the silver sources used for the coinage.

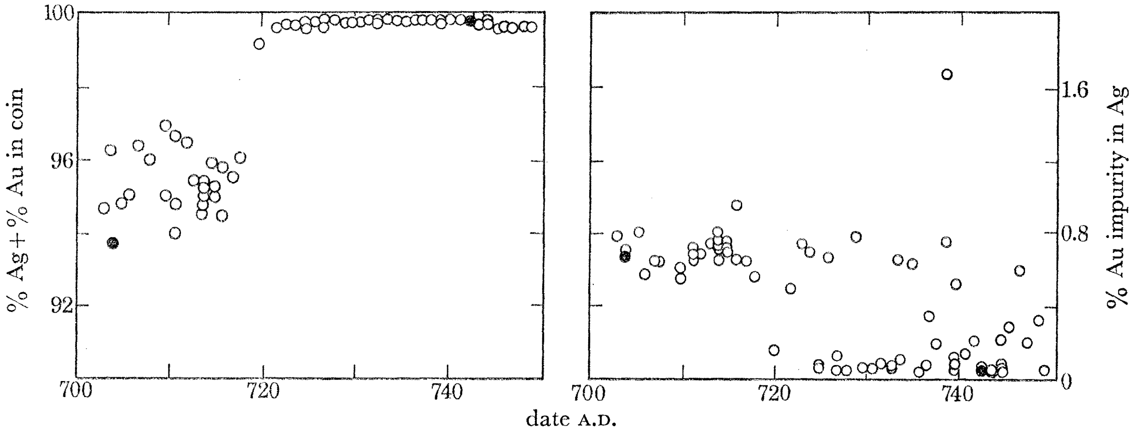

Figure 7. Silver plus gold contents of coins from the Umayyad mint of Wasit and the corresponding percentage gold impurity in the silver for each coin. Closed circles are based on chemical analysis data (Caley 1957).

Analyses are therefore performed for the relative amounts of gold, copper, and silver in the streaks; streaks of standards of known Au, Cu, and Ag content are irradiated together with those from the coins in order to obtain radioactivity calibrations for each irradiation. It is then assumed that the percentage Au plus percentage Cu plus percentage Ag equals 100. The intended silver content of the coin is assumed equal to 100 minus the percentage copper. The percentage Au in the silver is calculated as another important quantity. Data of this type for Umayyad coins from two mints are shown in figures 7 and 8.

The data for the coins from the mint at Wasit, which was located at what is now approximately the border between Iran and Iraq, showed a marked improvement in quality starting with the beginning of the reign of Hisham. Three possible reasons can be given for this improvement: (1) It was the result of a deliberate decision. (2) It was the result of improvements in the refining methods for removing any copper present in the silver ores. (3) It was due to the use of silver ore from a different source that had less copper impurity.

Reason (2) can be rejected since neither data for Damascus, figure 8, nor data from all other Umayyad mints show the same improvement in fineness as found for Wasit. Reason (3) can be rejected because a number of coins minted at Wasit after A.D. 720 were made from silver from the same silver source as was used for many of the coins struck before A.D. 720, as is seen in the right-handed graph of figure 7.

The early data from Wasit suggest the use of silver having about 0.7 % gold impurity. Around A.D. 720 another silver source having less than 1 % gold impurity was mainly used, although occasional coins were struck using silver having 0.7 % Au. Intermediate gold contents are either mixtures of the two types of silver, mixtures of the new bullion with melted down older coins, and/or an occasional use of silver ore from another source such as the coin having 1.7 % gold.

Data from other mints show different patterns. For example, silver with less than 1 % gold was being used by mints to the north of Wasit at least 10 years before its use in Wasit. Apparently the source of this silver ore lies in that general direction. Damascus, on the other hand, did not use the silver ore with less than 1 % gold. The ores its mint used have about 0.7, 0.9, 1.1, and 1.4 to 1.6 % gold. Mints in the northeast region of Persia used silver usually having more than 1 % gold.

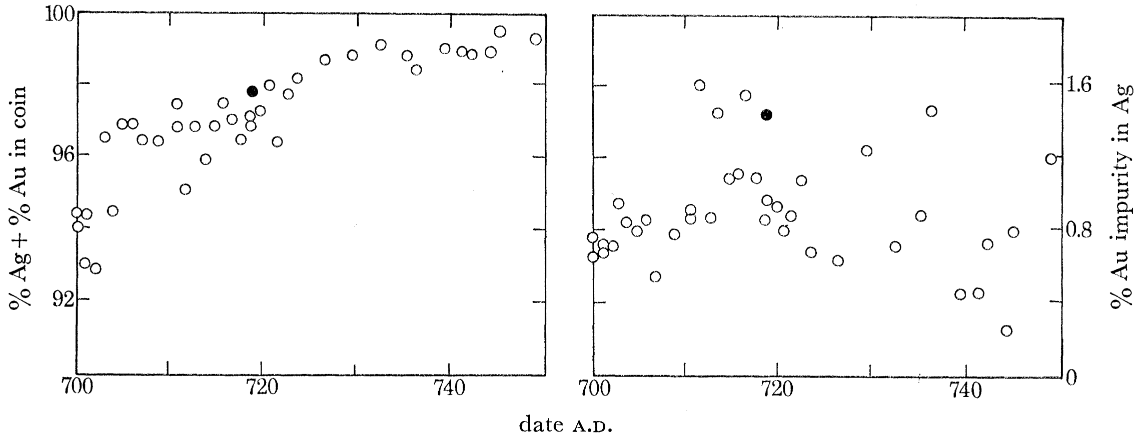

Figure 8. Data similar to that of figure 7 except for the Umayyad mint of Damascus.

In a few cases, historians have been in doubt about the location of a few of the Umayyad mints—and many of the Sasanian mints. These data indicating the type of silver in use have assisted in defining the geographical regions in which these mints were located.

The type of data presented here also has other uses. Historians can determine, from the silver fineness of the coins produced at each mint, the extent of control a monarch exercised over the various regions of his kingdom.

In addition, data of this type assist in the identification of modern coin forgeries. If the forgery was made of modern silver, the gold content would be almost zero since present-day silver is highly refined. This application of the method is particularly suited to the analysis of silver art objects.

SASANIAN ART OBJECTS

Many museums possess silver plates, bowls, and figures attributed to the Sasanian period. A number of these objects show a Sasanian king, usually on horseback, hunting boar. A few historians have suggested that some, and perhaps many of these objects were manufactured in post-Sasanian periods since the later dynasties have glorified the Sasanian era.

Our streak analyses of over 400 Sasanian coins have shown that virtually all were made from silver having between 0.4 and 0.9 % gold. Only two of the coins had more than 1 % gold and these contents were only 1.1 %.

Of the 55 Sasanian silver art objects we have analysed by the streak method, a number have gold impurity levels in excess of 1 %, and on occasion the gold level is as great as 1.5 to 2.0 %. These objects clearly were not manufactured in the Sasanian kingdom. The only Islamic period during which high gold-content silver is used in coinage is during the Umayyad period

Corinth and Athens during the period of the seventh to the fifth centuries B.C. depend to a considerable extent on the extremely wide distribution of Corinthian and Athenian fine pottery, and the ease with which the work of the two cities can be distinguished from each other by reasoning based on criteria of typology and style about which there is no disagreement. Both cities had their imitators, particularly in Italy, but the imitations are also readily distinguishable for what they are. There is no case in this set of circumstances for calling on laboratory aid to solve problems of identity.

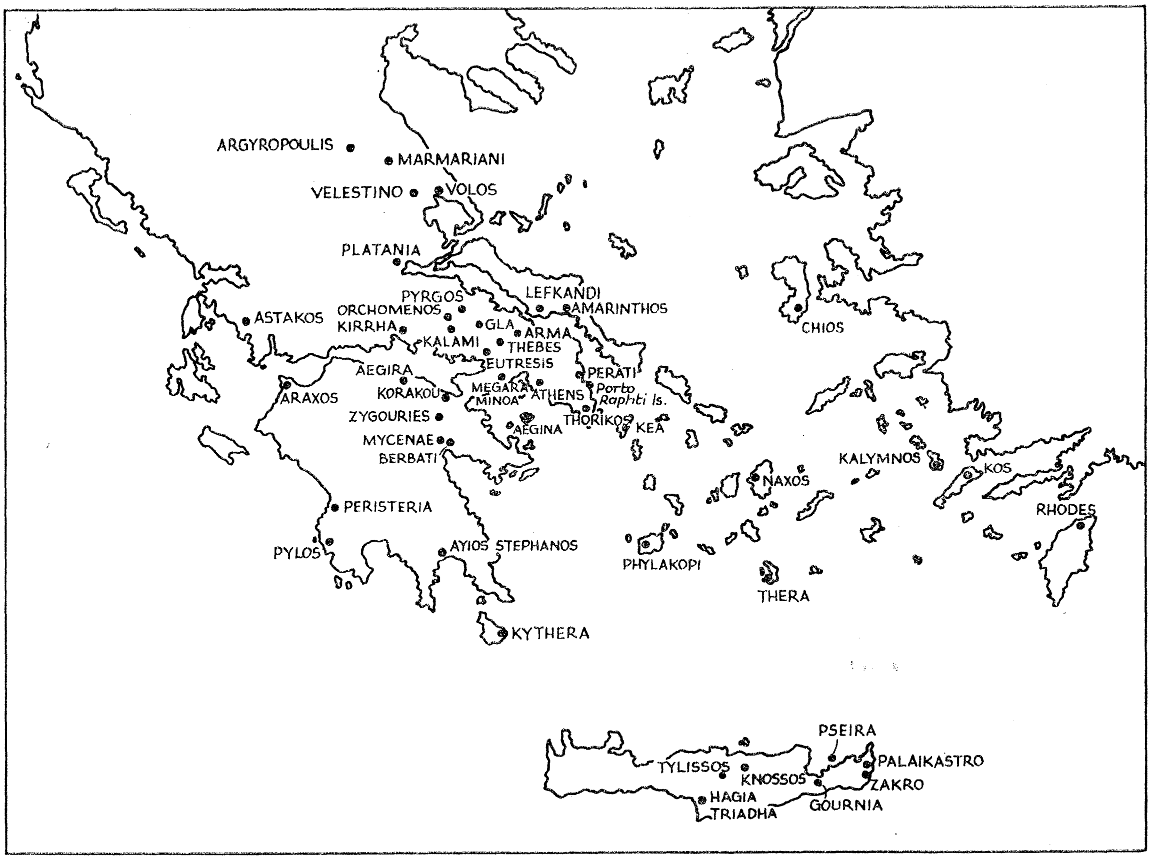

FIGURE 1. Location of sites from which pottery has been sampled.

Fine pottery that earned the esteem of a wide foreign market was produced in Greece much earlier than this, however. In the Late Bronze Age the people in Greece whom we call the Mycenaeans took on a huge share of the cultural identity of their much more advanced contemporaries in Crete, the Minoans. Mycenaean potters shared in this process, the result of which—and here I have somewhat to simplify—was the production over a very wide area including Greece from the Gulf of Pagasae south, Crete and the other Greek islands of fine painted pottery which has far more points of similarity than of difference. After the beginning of the fourteenth century B.C. the importance of Crete waned, but for the next 200 years, potters in Greece and the islands, especially the Dodecanese, continued making fine wares that exhibit a remarkable unity of form and style, and certainly cannot be attributed to particular production centres by conventional archaeological methods. There was no shortage of foreign custom for this Mycenaean pottery; Italy, Sicily, the Troad, the west coast of Asia Minor, Cyprus, Syria and Palestine and Egypt all acquired varying amounts of this pottery. In some cases, particularly in Cyprus, the quantities are enormous, and have led to speculation about the establishment of colonies rather than the maintainance of trade.

Here, then, were innumerable problems of identity to be answered, problems which could not be solved by typological and stylistic reasoning alone. Some of them were involved with the distinction between what is Minoan and what is Mycenaean; some are concerned with the hypothesis of Mycenaean potters working overseas, particularly in Cyprus, others with the source(s) of specific classes of pottery, of which we may quote Mycenaean pictorial pottery and stirrup jars painted with linear B inscriptions as particularly vexed questions. In short, the situation is one particularly well suited to an analytical method capable of calculating quantitatively the trace elements in large numbers of pottery samples.

The method chosen—not the only one possible—was optical emission spectroscopy, by which a minute specially prepared sample is burnt and the resulting spectra recorded in a photographic plate. These spectra vary in intensity in a measureable degree which permits judgements to be made about the quantitative differences in the trace elements present as between one sample and another, or between a set of samples from one provenance and a set from another.

There are two parts to the laboratory investigation.

(1) The establishment of controls for the producing areas, so that data are collected from as many as possible of the sites where Minoan and Mycenaean pottery was produced.

These controls establish the identities of distinct types of pottery composition, and the areas to which they belong. I say 'areas' advisedly, since it sometimes happens that the same composition type is found widely distributed over a very large area. This proved to be the case with many of the sites studied in the Peloponnese, for example. Conversely, it happens that a unique composition type is identified at a single site of trivial consequence, as in the case of Platania in the Spercheios Valley in Greece. It is a particularly tiresome feature of this investigation that the location of different composition types should be so arbitrary.

(2) The recognition of a particular archaeological problem to the solution of which the composition data from the controls can be applied. The simplest type of problem suitable for this treatment is probably one concerned with the source of manufacture of Minoan or Mycenaean pottery found outside the producing areas. Problems within the producing areas tend to greater complexity, and present certain difficulties of their own. It has been our experience in general that some hard in-fighting may be needed to gain any sort of acceptance for results which prove unexpected and unwelcome. Though this is no doubt as it should be, there must be a limit to the occasions on which an investigation such as this should be expected to rehearse and defend the basic assumptions on which it rests, unless, of course, it is assailed by entirely new objections.

What has this investigation so far achieved? Mrs Richards and Mrs Millett between them have isolated nearly twenty different composition types in the producing areas. It has been shown that the Mycenaean pottery found in Egypt in the ruins of Akhnaten's palace at Tell el Amarna was made somewhere in the Peloponnese. The pictorial Mycenaean pottery from Cyprus, thought by some to have been made in Cyprus itself, also comes from the Peloponnese. Imitation Mycenaean pottery, however, *was* made in Cyprus, and in more than one place. The stirrup jars with painted inscriptions in linear B found at Thebes in Boeotia proved to have been made in several places—a majority could be attributed to a site, or sites, in east Crete, while a smaller number had been manufactured in Greece.

Very recently the so-called Swallow Vases from the island of Thera (Santorin) have been investigated. This was done on behalf of Professor Spyridon Marinatos, Director-General of Antiquities in Greece, and excavator of the Late Bronze Age settlement site at Akrotiri on Thera. I am grateful to Professor Marinatos for allowing mention to be made of the results. Thera has proved to have a composition type of its own, and the Swallow Vases samples conform to it; it is therefore evident that these vases were made in Thera itself. It is hoped in the future to take samples from the other vases of this class found outside Thera to determine whether all came from this common source or not.